

# CHEMICAL THERMODYNAMICS

## 5.0 INTRODUCTION :

Thermo (Heat/energy) + Dynamics (Flow/motion)

**Thermodynamics** is the branch of science which deals with the energy changes taking place in all physical and chemical processes but **Chemical thermodynamics** is the branch of thermodynamics which deals with the study of energy changes taking place in chemical processes.

### Advantages of thermodynamics :

- (i) It gives information about various **thermodynamic laws**.
- (ii) It helps us to predict whether a given **chemical reaction will take place or not** under the given set of conditions.
- (iii) It gives information about various **energy changes**.

### Limitations of thermodynamics :

- (i) Thermodynamics deals with the properties like temperature, pressure, volume, etc of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

or

Thermodynamics deals with **macroscopic system** but not with **microscopic system**.

- (ii) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the **rate of reaction**.

## 5.1 SOME IMPORTANT TERMS :

- **System** : A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation
- **Surrounding** : The rest part of the universe excluding the system is called surrounding.  
Universe = System + Surrounding
- **Boundary** : Anything which separates system and surrounding is called boundary.

### Types of boundary :

- (i) Boundary can be conducting or non-conducting.
- (ii) Boundary can be rigid or non-rigid.
- (iii) Boundary can be real or imaginary.

### For example :

A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and anything which is outside the beaker is called surroundings.

## 5.2 TYPES OF SYSTEM :

### System are of 3 types :

**Open system** : This type of system can exchange energy as well as matter with the surrounding. The boundary is neither sealed nor insulated. Total mass will not remain constant.

**Eg.1** Coffee in open glass. Hot water in open glass.

**Eg.2** All living systems. human being, plants, animals.

**Eg.3** Classroom, earth.



**Closed system :** This type of systems can exchange energy, (in the form of heat, work or radiations) but not matter with its surroundings. The boundary is sealed but not insulated. Amount of the system will remain constant.

**Eg.1** Coffee in closed vessel. Hot water in closed vessel.

**Eg.2** Glowing bulb, tube light.

**Eg.3** A satellite in orbit.

**Isolated system :** This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

**Eg.1** Coffee in thermosflask.

### 5.3 STATE OF THE SYSTEM :

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.
- The state of the system is defined by their measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

#### State Function :

- Those state variables which depend only upon initial and final state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

**Ex.** E, H, S, G, T, P, V etc.

#### Path function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

**Eg.** Work done (w), heat (q)

#### Thermodynamic properties :

- Intensive properties :** The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.
- Extensive properties :** The properties of the system which are dependent on matter (size and mass) present in system are called extensive properties

Extensive Properties	Intensive Properties
Volume (V)	Molar volume ( $V_m$ )
Number of moles (n)	Density (d)
Mass (m)	Gibb's energy per mole ( $G_m$ )
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M,N)
Heat capacity (C)	Boiling point, freezing point ( $T_b$ , $T_f$ )
Force (F)	Cell potential ( $E_{cell}$ )
Surface Area (A)	Specific conductance ( $\kappa$ )
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure



### Special Points :

- (i) The ratio of two extensive properties indicates the intensive property Eg.  $d = \frac{\text{mass}}{\text{volume}}$
- (ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

Eg. Mass per unit volume = density;  $\left(d = \frac{m}{V}\right)$

- (iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

	<div>H<sub>2</sub>O</div>	<div>H<sub>2</sub>O</div>	On adding
Vessel	A	B	
Mass	$m_1$	$m_2$	$m_1 + m_2$ (Total mass)
Moles	$n_1$	$n_2$	$n_1 + n_2$ (Total moles)
Volume	$V_1$	$V_2$	$V_1 + V_2$ (Total volume)
Density	$d$	$d$	Remains same (d)
Boiling point	$T$	$T$	Remains same (T)

## 5.4 TYPES OF THERMODYNAMIC PROCESSES :

When a system changes from one state to another, the operation is called a thermodynamic process.

Thermodynamic processes may be in form of expansion or compression.

### (a) Isothermal Process ( $n, T = \text{constant}$ )

Isothermal processes are those processes in which

- (a) Temperature of system during entire process remains constant i.e.  $\Delta T = 0$
- (b) Heat is exchanged with surroundings
- (c) Volume and pressure are variable
- For ideal gas in Isothermal process  $\Delta E = 0$  and  $\Delta H = 0$
- All phase transitions are isothermal process but  $\Delta E \neq 0$  and  $\Delta H \neq 0$

### (b) Isobaric Process ( $n, P = \text{constant}$ ) :

Isobaric processes are those processes in which

- (a) Pressure of system during entire process remains const i.e.  $\Delta P = 0$
- (b) Volume and temperature are variable.
- (c) Process in open system is isobaric in nature.

### (c) Isochoric Process ( $n, V = \text{constant}$ ) :

Isochoric processes are those processes in which

- (a) Volume remains constant i.e.  $\Delta V = 0$
- (b) Pressure and temperature are variable
- (c) Work,  $w = -P\Delta V$ ,  $\therefore \Delta V = 0$ ,  $\therefore w = 0$  (Zero)
- (d) Process in closed system is isochoric in nature.

### (d) Adiabatic Process ( $n = \text{constant}, q = 0$ )

Adiabatic processes are those processes in which

- (a) No exchange of heat between system and surrounding takes place during entire process i.e.  $q = 0$
- (b) The temperature pressure, volume of the system varies.
- (c) The system is thermally insulated by keeping the system in an insulated container.



**(e) Cyclic Process :**

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

**In cyclic process change in all state function will be zero.** i.e.  $\Delta E = 0$ ,  $\Delta H = 0$ ,  $\Delta P = 0$ ,  $\Delta T = 0$

**(f) Reversible Process (quasi-static) :**

- (1) Process in which all changes occurring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.
- (2) Driving force should be infinitesimally greater than opposing force.
- (3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.
- (4) It is an ideal process.
- (5) Work obtained in expansion is maximum.
- (6) System is in virtual equilibrium at any state.
- (7)  $P_{\text{ext}} = P_{\text{int}} \pm dP$  ;  $P_{\text{ext}}$  is variable.

**Irreversible Process :**

- (1) Process in which direction of change cannot be reversed by small changes in variables.
- (2) Driving force is much greater than opposing force.
- (3) It takes finite time and finite/usually single step.
- (4) Process takes place in short time
- (5) All natural processes are irreversible
- (6) System is in equilibrium only at initial and final state
- (7)  $P_{\text{ext}} = P_{\text{int}} \pm \Delta P$  ;  $P_{\text{ext}}$  is constant.

## 5.5 WORK AND HEAT :

**(A) Work :** Product of force and displacement is known as work.

$$\text{work (w)} = \text{force (F)} \times \text{displacement (}\ell\text{)}$$

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose area of cross section of cylinder = A and pressure on the piston = P

Initial volume of the gas =  $V_1$  and final volume of the gas =  $V_2$

(By expansion) displacement of piston =  $\ell$

work done by the gas (in expansion) =  $w = F \cdot \ell$

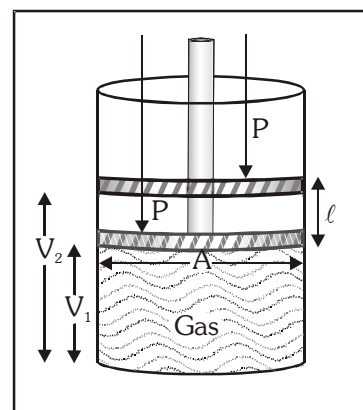
$$\therefore P = \frac{F}{A} \quad \therefore F = P \times A$$

$$w = P \times A \times \ell \text{ (change in volume} = A \times \ell = V_2 - V_1\text{)}$$

$$w = P \times (V_2 - V_1)$$

$$w = P\Delta V \text{ (According to Physics)}$$

In general  $w = -P_{\text{external}} \Delta V$  (According to Chemistry)



### SIGN CONVERSIONS :

- According to latest sign conventions
  - Work done is taken negative if it is done by the system since energy of system is decreased.  
**Eg.** Expansion of gas.  
 $\therefore V_2 > V_1$  ;  $\Delta V = \text{positive}$ ;  $w = \text{negative}$
  - Work done is taken positive if it is done on the system, since energy of system is increased.  
**Eg.** Compression work.  
 $\therefore V_1 > V_2$  ;  $\Delta V = \text{negative}$  ;  $w = \text{positive}$

### (B) Heat exchange (q) :

Heat is defined as the energy that flow in or out of a system because of a difference in temperature between the thermodynamic system and its surrounding. It is a path function.

According to IUPAC convention, heat given by the system is expressed with negative sign and heat given to the system is expressed with positive sign.

- Heat always flows from high temperature to low temperature.
- Heat flowing into the system  $q = \text{positive}$
- Heat flowing out of the system  $q = \text{negative}$

### Units of heat & work :

**Calorie :** It is defined as the quantity of heat required to raise the temperature of 1 g of water by  $1^\circ\text{C}$  (14.5 to 15.5 $^\circ\text{C}$ )

$$1 \text{ cal} = 4.184 \text{ J} \simeq 4.2 \text{ J}$$

$$1 \text{ L-atm} = 101.3 \text{ J} = 24,206 \text{ cal} = 101.3 \times 10^7 \text{ erg}$$

$$1 \text{ L-atm} > 1 \text{ Cal} > 1 \text{ J} > 1 \text{ erg}$$

### GOLDEN KEY POINTS

- Molar properties like  $\Delta H_m$ ,  $\Delta G_m$ ,  $\Delta S_m$ ,  $\Delta U_m$  are intensive properties.
- In cyclic process change in all state function will be equal to zero.  
 $\Delta E = 0$ ;  $\Delta H = 0$   $\Delta P = 0$ ,  $\Delta T = 0$  etc.
- For ideal gases  $\Delta E = 0$  (For isothermal process)
- All natural process are irreversible in nature.
- Both  $q$  and  $w$  are (+) **to** system.
- Both  $q$  and  $w$  are (–) **by** the system.

### Illustrations

**Illustration 1.** Find the work done in each case :

- When one mol of ideal gas in 10 litre container at 1 atm is allowed to enter a **vacuum bulb** of capacity 100 litre.
- When 1 mol of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

**Solution**

(a)  $W = -P\Delta V$  but since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called **free expansion** and work done is zero.

**Note :-** Work done in free expansion is always zero.

(b)  $W = -P\Delta V = -1(5 - 1) = -4 \text{ L-atm}$ .



**Illustration 2.** A 5 litre cylinder contained 10 mol of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmosphere pressure is 1.0 atm. Calculate the work done by the gas ? ( $R = 0.083 \text{ lit atm mol}^{-1} \text{ K}^{-1}$ )

**Solution**

$$V_{\text{initial}} = 5 \text{ L}$$

$$T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$V_{\text{final}} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 249 - 5 = 244 \text{ L}$$

$$W_{\text{exp}} = -P\Delta V = -1 \times 244 \text{ L-atm.} = -244 \text{ L-atm.}$$

### BEGINNER'S BOX-1

- Which of the following open system  
(1) Animals and plants      (2) A fridge      (3) A solar cooker      (4) None of these
- One mole of gas occupying 3 litre volume is expanded against a constant external pressure of one atm to a volume of 15 litre. The work done by the system is :-  
(1)  $-1.215 \times 10^3 \text{ J}$       (2)  $+12.15 \times 10^3 \text{ J}$       (3)  $+121.5 \times 10^3 \text{ J}$       (4)  $+1.215 \times 10^3 \text{ J}$
- The work done during the expansion of a gas from a volume of 4 dm<sup>3</sup> to 6 dm<sup>3</sup> against a constant external pressure of 3 atm is :-  
(1) -608 J      (2) +304 J      (3) -304 J      (4) -6 J
- The work done during the expansion of a gas from a volume of 14 dm<sup>3</sup> to 16 dm<sup>3</sup> against a constant external pressure of 2 atm is :-  
(1) -405.2 J      (2) +304 J      (3) -304 J      (4) -6 J

## 5.6 INTERNAL ENERGY (E/U) :

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translatory, rotatory and vibratory motion), electronic energy, nuclear energy etc.

$$E = E_{\text{PE}} + E_{\text{T}} + E_{\text{R}} + E_{\text{V}} + E_{\text{e}} + E_{\text{N}}$$

(i) Internal energy is an **extensive property**.

(ii) We can **never find out the absolute value** of internal energy (E) of system.

We can only calculate the change in internal energy of the system ( $\Delta E$ ) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a **state function**.

$$\Delta E = E_f - E_i$$

$$(\text{In reaction}) \quad \Delta E = E_p - E_R$$

$$\Delta E \text{ is + ve if } E_f > E_i$$

$$\Delta E \text{ is - ve if } E_f < E_i$$



## 5.7 LAWS OF THERMODYNAMICS :

### GENERAL POINT :

Laws of thermodynamics are based on human experiences there is no formal proof for them.

### FIRST LAW OF THERMODYNAMICS (FLOT) :

- This law is based on law of conservation of energy and was given by **Robert Mayer and Helmholtz**.
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system is always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

$$\boxed{\Delta E = q + w} : \text{where } q, w \text{ are path function and } E \text{ is state function.}$$

Here  $q$  is the energy given to the system and  $w$  is the work done on the system ;  $\Delta E$  is change in internal energy.

**Note** :- Put the value of  $q$  and  $w$  with proper sign.

### CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS :

#### (a) During isothermal process of an ideal gas :

During an isothermal process the temperature of the system remains constant and hence

$$\Delta E = 0$$

Therefore FLOT :  $\Delta E = q + w$

$$\therefore \boxed{+q = -w} \text{ or } -q = +w$$

In isothermal process –

(I) Heat absorbed by the system is equal to work done by the system.

**OR**

(II) Heat evolved by the system is equal to work done on the system.

#### (b) During isochoric process :

At constant volume  $V_1 = V_2$  i.e.  $\Delta V = 0$

Hence  $W = -P\Delta V = 0$  ..... No work done at constant volume therefore,

$$\text{FLOT: } \Delta E = q + w \quad \boxed{\Delta E = q_v}$$

(i) In isochoric process

- At constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

**OR**

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume ( $q_v$ ) =  $\Delta E$

(iii) **In isochoric process heat is independent of path.**



**(c) During adiabatic process :**

During adiabatic process the system acts an isolated system and hence  $q = 0$  in such cases. Therefore

$$\text{FLOT : } \Delta E = q + w \quad \because q = 0 \quad \boxed{\Delta E = w}$$

- (i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

**OR**

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

- (ii) **In adiabatic process work is independent of path.**

**(d) During Cyclic Process :**

$$\Delta E = 0 \quad \text{FLOT ; } \Delta E = q + w \quad \boxed{+q = -w}$$

**In cyclic process.**

- (I) Work done by the system is equal to heat absorbed by the system.

**OR**

- (II) Work done on the system is equal to heat evolved by the system.

**(e) During Isobaric process :**

$P = \text{constant}$

$$\text{FLOT : } \Delta E = q + W$$

$$\Delta E = q + (-P\Delta V)$$

$$q_p = \Delta E + P\Delta V$$

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$q_p = (E_2 + PV_2) - (E_1 + PV_1)$$

$$\therefore \text{ Enthalpy } H = E + PV$$

$$\therefore q_p = H_2 - H_1 \quad \boxed{q_p = \Delta H}$$

- (i) **In isobaric process :**

- At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system.

**OR**

- At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

- (ii) Heat at constant pressure ( $q_p$ ) =  $\Delta H$

- (iii) **In isobaric process heat is independent of path.**





## Illustrations

**Illustration 3.** 1g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporisation at this pressure is 540 Cal/g. Find the increase in internal energy of water. (1 L atm = 101 J)

**Solution** Work done  $w = -P\Delta V = -P(V_2 - V_1)$

$$= -1(1671 - 1) \times \frac{1}{1000} = \frac{-1670}{1000} \text{ L-atm}$$

$$= \frac{-1670}{1000} \times 101 \text{ J} = -168.67 \text{ J}$$

given that  $q = 540 \text{ Cal} = 540 \times 4.2 \text{ J} = 2268 \text{ J}$

$\therefore \Delta E = q + w = 2268 - 168.67 = 2099.33 \text{ J}$

**Illustration 4.** A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy.

**Solution**  $w = -P\Delta V = -1 \times (2.5 - 2) = -0.5 \text{ L-atm}$  or  $w = -0.5 \times 101.3 = -50.65 \text{ J}$ .

$\Delta E = q + w = 300 + (-50.65)$

$\Delta E = 249.35 \text{ J}$

**Illustration 5.** A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surroundings. Calculate the change in internal energy of the system.

**Solution** During the process,

$q = 600 \text{ J}$ ,  $\Delta V = 12 - 2 = 10 \text{ L}$ ,  $P = 1 \text{ atm}$

$w = -P\Delta V$

$= -1 \times 10 = -10 \text{ L atm}$

Now,  $1 \text{ L atm} = 101.3 \text{ J}$

$\therefore w = -10 \times 101.3 = -1013 \text{ J}$

According to first law of thermodynamics,

$\Delta E = q + w = 600 - 1013 = -413 \text{ J}$

**Illustration 6.** Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant external pressure of 4 atm. Calculate  $q$ ,  $w$  &  $\Delta E$ . ( $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$ )

**Solution** Work done on the system,

$w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$

$V_i = \frac{nRT}{P}$

$n = 2 \text{ mol}$  and  $R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$ ,

$T = 273 + 27 = 300 \text{ K}$ ,  $P = 2 \text{ atm}$

$V_i = \frac{2 \times 0.082 \times 300}{2} = 24.6 \text{ L}$  and  $V_f = \frac{V_i}{2} = \frac{24.6}{2} = 12.3 \text{ L}$



$$w = -4 \text{ atm} \times (12.3 - 24.6) \text{ L} = 49.2 \text{ L atm} = 49.2 \times 101.3 \text{ J} = 4984 \text{ J}.$$

Since, it is isothermal compression,  $\Delta E = 0$

Now,  $\Delta E = q + w$

$$0 = q + 4984 \text{ J or } q = -4984 \text{ J}$$

**Illustration 7** A system is provided with 100 J of heat. Work done on the system is 20 J. What is the change in internal energy.

**Solution**  $q = 100 \text{ J}$  and  $w = +20 \text{ J}$   
 $\Delta E = q + w = 100 + 20 \text{ J} = 120 \text{ J}$

**Illustration 8.** An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect Vacuum. If a hole is opened between the two portions, Calculate the –

(i) Change in internal energy of the gas (ii) Change in temperature of the gas

**Solution** For insulated system,  $q = 0$

The gas is allowed to expand against vacuum, the process of free expansion and thus

$$w = -P\Delta V = 0 \text{ (for vacuum } = P_{\text{ext}} = 0)$$

$$\text{Thus from I law of thermodynamics, } \Delta E = q + w \text{ or } \Delta E = 0$$

i.e. internal energy change is zero or internal energy of gas remains constant during free expansion.

Also  $E \propto T$  and thus temperature of the gas will also remains constant.

### BEGINNER'S BOX-2

- A system absorb 300 cal of heat with the result of that, the volume of the system becomes double of its initial volume and temperature changes from 273K to 546K. The work done by the system on the surroundings is 200.0 Cal Calculate  $\Delta E$  :-  
 (1) 273 kCal (2) 500 Cal (3) 100 Cal (4) -500 Cal
- One mol of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The  $\Delta E$  for the process is :- ( $R = 2 \text{ Cal K}^{-1} \text{ mol}^{-1}$ )  
 (1) 163.7 Cal (2) 1381.1 Cal (3) 9 L-atm (4) Zero
- In an adiabatic process which of the following is true :-  
 (1)  $q = +w$  (2)  $-\Delta E = -w$  (3)  $P\Delta V = 0$  (4)  $q = \Delta E$
- In an isochoric process, the increase in internal energy is :-  
 (1) Equal to the heat absorbed (2) Equal to the heat evolved  
 (3) Equal to the work done (4) Equal to zero



## 5.8 ENTHALPY (H) :

Mathematically it is heat contained in the system measured at constant pressure.

The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

$$\boxed{H = E + PV}$$

- It is impossible to determine absolute value of enthalpy so we determine change in enthalpy ( $\Delta H$ ).

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

- Enthalpy is an extensive property because E and V are extensive properties.
- It is a state function because E, P and V are state functions.

$$\therefore H = E + PV$$

$$\therefore \boxed{\Delta H = \Delta E + \Delta(PV)} \dots(i)$$

(when P, V and T are variables)

$$\text{At constant pressure : } \boxed{\Delta H = \Delta E + P.\Delta V} \dots(ii)$$

$$\text{At constant volume : } \boxed{\Delta H = \Delta E + V.\Delta P} \dots(iii)$$

For chemical reactions at constant temperature and pressure  $\therefore P.\Delta V = \Delta n_g RT$

$$\text{So from equation (i)} \quad \boxed{\Delta H = \Delta E + \Delta n_g RT} \dots(iv)$$

where  $\Delta H = q_p$  ; at constant P ;  $\Delta E = q_v$  ; at constant V

$$\text{So equation (iv) can be also written as } \boxed{q_p = q_v + \Delta n_g RT} \dots(v)$$

### GOLDEN KEY POINTS

- If,  $\Delta n_g = 0 \rightarrow \boxed{\Delta H = \Delta E}$  eg.  $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If,  $\Delta n_g > 0 \rightarrow \boxed{\Delta H > \Delta E}$  eg.  $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If,  $\Delta n_g < 0 \rightarrow \boxed{\Delta H < \Delta E}$  eg.  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

## Illustrations

**Illustration 9.** The heat of reaction for  $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$  at constant volume is  $-1228.2 \text{ kCal}$  at  $25^\circ\text{C}$ . Calculate the heat of reaction at constant pressure and at  $25^\circ\text{C}$ .

**Solution**

$$\Delta n_g = [10] - [12] = -2$$

$$\Delta H = \Delta E + \Delta n_g RT$$

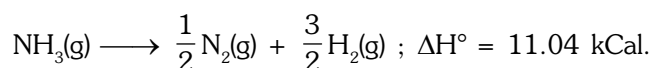
$$= -1228.2 \times 10^3 + (-2)(2) \times 298$$

$$= -1229392 \text{ Cal}$$

$$\Delta H = -1229.392 \text{ kCal}$$



**Illustration 10.** For the reaction at 25°C



Calculate  $\Delta E^\circ$  of the reaction at the given temperature.

**Solution**

$$\Delta H^\circ = \Delta E^\circ + \Delta n_g RT$$

$$\Delta n_g = 2 - 1 = 1 \text{ mol}$$

$$\Delta E^\circ = \Delta H^\circ - \Delta n_g RT$$

$$= 11.04 \text{ Kcal} - 1 \text{ mol} \times \frac{2}{1000} \text{ kCal mol}^{-1} \text{K}^{-1} \times 298 \text{K}$$

$$= 11.04 - 0.596 = 10.44 \text{ kCal}$$

**Illustration 11** At 27°C the internal energy change of reaction  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$  is 2Cal. What is the enthalpy change of this reaction.

**Solution**

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta H = \Delta E + 0 \times RT$$

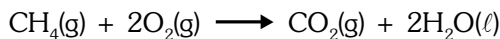
$$\Delta H = \Delta E$$

$$\Delta H = 2\text{Cal}$$

**Illustration 12** The heat of combustion of gaseous methane ( $\text{CH}_4$ ) at constant volume is measured in bomb calorimeter at 298K is found to be  $-885.4 \text{ kJ mol}^{-1}$ . Find the value of enthalpy change at the same temperature.

**Solution**

Combustion of methane gives  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\ell)$  as



$$\Delta E = -885.4 \text{ kJ mol}^{-1} = -885400 \text{ J mol}^{-1}$$

$$\Delta n_g = 1 - (1 + 2) = -2 \text{ mol}$$

$$T = 298\text{K}, R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\text{Now, } \Delta H = \Delta E + \Delta n_g RT$$

$$= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{K}^{-1}) \times (298\text{K})$$

$$= -885400 - 4955$$

$$= -890355 = -890.355 \text{ kJ}$$

**Illustration 13.** The enthalpy change ( $\Delta H$ ) for the reaction :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  is  $-92.38 \text{ kJ}$  at 298 K. What is  $\Delta E$  at 298 K ?

**Solution**

$$\Delta H \text{ and } \Delta E \text{ are related as } \Delta H = \Delta E + \Delta n_g RT$$

$$\text{for the reaction, } \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$$

$$\Delta n_g = 2 - (1 + 3) = -2 \text{ mol}, T = 298 \text{ K}$$

$$\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{K}^{-1}) \times (298 \text{ K})$$

$$-92380 = \Delta E - 4955$$

$$\Delta E = -92380 + 4955$$

$$= -87425 \text{ J} = -87.425 \text{ kJ.}$$



**Illustration 14** The enthalpy change for the reaction  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  at 1000K is  $176 \text{ kJ mol}^{-1}$ . Calculate the change in internal energy.

**Solution**  $\Delta H = \Delta E + \Delta n_g RT$   
 $176 = \Delta E + (+1) \times 8.314 \times 10^{-3} \times 1000$   
 $\Delta E = 167.686 \text{ kJ}$

### BEGINNER'S BOX-3

- When a solid melts, there is :-  
 (1) No increase in enthalpy (2) Increase in enthalpy  
 (3) Decrease in enthalpy (4) Anything can happen
- For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$  which of the following is valid :-  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H < \Delta E$   
 (3)  $\Delta H > \Delta E$  (4) None of these
- Heat exchanged in a chemical reaction at constant pressure is called :-  
 (1) Internal energy (2) Enthalpy  
 (3) Entropy (4) Free energy
- Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is  $10.0 \text{ kCal mol}^{-1}$ . What will be the change in internal energy of 3 mol of liquid at same temperature and pressure  
 (1) 13.0 kCal (2) -13.0 kCal  
 (3) 27.0 kCal (4) -27.0 kCal
- What is the value of  $\Delta n_g$  if we consider the combustion of 1 mol of liquid ethanol if reactants and products are at 298 K :-  
 (1) -1 (2) -2 (3) +1 (4) +2
- If a reaction involves only solids and liquids, which of the following is true  
 (1)  $\Delta H < \Delta E$  (2)  $\Delta H = \Delta E$   
 (3)  $\Delta H > \Delta E$  (4)  $\Delta H = \Delta E + RT\Delta n_g$
- The value of  $\Delta H - \Delta E$  for the following reaction at  $27^\circ\text{C}$  will be,  $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  :-  
 (1)  $8.314 \times 273 \times (-2) \text{ J}$   
 (2)  $8.314 \times 300 \times (-2) \text{ J}$   
 (3)  $8.314 \times 27 (+2) \text{ J}$   
 (4)  $8.314 \times 300 (+2) \text{ J}$
- At constant temperature for the reaction  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell)$ ,  $\Delta E - \Delta H$  is :-  
 (1) +RT (2) -3RT (3) +3RT (4) -RT



## 5.9 HEAT CAPACITY / MOLAR HEAT CAPACITY / SPECIFIC HEAT CAPACITY :

- (i) **Heat capacity (C)** : Amount of heat required to raise the temperature of given amount of a substance by 1°C or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

$$C = \frac{dq}{dT}$$

**Units :-** JK<sup>-1</sup>, Cal K<sup>-1</sup>, J °C<sup>-1</sup>, Cal °C<sup>-1</sup>

- Heat capacity is extensive property.

- (ii) **Molar heat capacity (C<sub>m</sub>)** : Amount of heat required to raise the temperature of 1 mole of substance by 1°C or 1 K is called as molar heat capacity.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow C_m = \frac{C}{n}$$

**Units :-** Jmol<sup>-1</sup> K<sup>-1</sup>, Cal mol<sup>-1</sup> K<sup>-1</sup>, J mol<sup>-1</sup> °C<sup>-1</sup>, Cal mol<sup>-1</sup> °C<sup>-1</sup>

- Molar heat capacity is an intensive property.

- (iii) **Specific heat capacity (c)** : Amount of heat required to raise the temperature of 1 g of substance by 1°C or 1K is called as specific heat capacity.

$$c = \frac{C_m}{\text{molecular weight}}$$

**Units :-** Jg<sup>-1</sup> K<sup>-1</sup>, Cal g<sup>-1</sup> K<sup>-1</sup>, J g<sup>-1</sup> °C<sup>-1</sup>, Cal g<sup>-1</sup> °C<sup>-1</sup>

- Specific heat capacity is an intensive property.

- If heat is supplied at constant pressure, then  $C_p = \left( \frac{dq}{dT} \right)_p = \frac{dH}{dT} \dots (i)$

- If heat is supplied at constant volume, then  $C_v = \left( \frac{dq}{dT} \right)_v = \frac{dE}{dT} \dots (ii)$

From equation (i) and (ii) :

From equation (i)	Unit	From equation (ii)
<ul style="list-style-type: none"> <li>ΔH = C<sub>p</sub>dT [Here C<sub>p</sub> is heat capacity at constant P]</li> <li>For n moles ΔH = nC<sub>p</sub>dT [Here C<sub>p</sub> is molar heat capacity at constant P]</li> <li>For m gram ΔH = mC<sub>p</sub>dT [Here C<sub>p</sub> is gram specific heat (specific heat capacity) at constant P]</li> </ul>	<p>JK<sup>-1</sup></p> <p>J mol<sup>-1</sup>K<sup>-1</sup></p> <p>J g<sup>-1</sup> K<sup>-1</sup></p>	<ul style="list-style-type: none"> <li>ΔE = C<sub>v</sub>dT [Here C<sub>v</sub> is heat capacity at constant V]</li> <li>ΔE = nC<sub>v</sub>dT [Here C<sub>v</sub> is molar heat capacity at constant V]</li> <li>ΔE = mC<sub>v</sub>dT [Here C<sub>v</sub> is gram specific heat (specific heat capacity) at constant V]</li> </ul>



**Relation between  $C_p$  and  $C_v$  for 1 mole of an ideal gas :**

$$\therefore H = E + PV$$

for ideal gas,

$$PV = nRT$$

$$PV = RT \quad \text{for 1 mole}$$

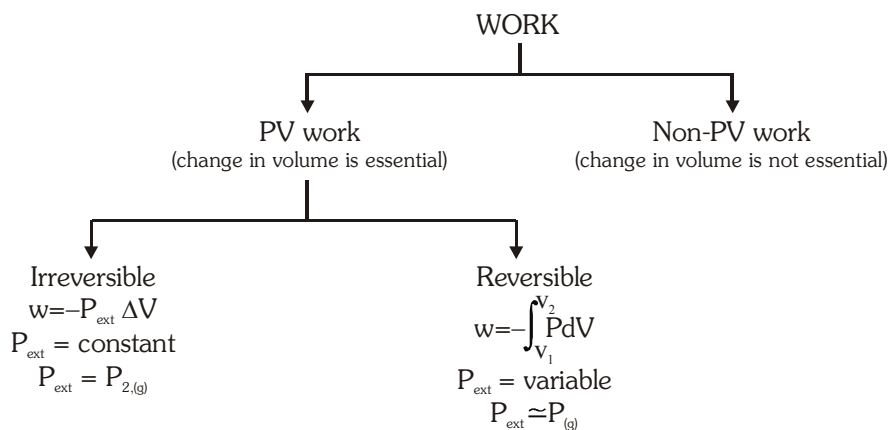
$$\therefore H = E + RT \text{ differentiate w.r.t. temperature}$$

$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) + R$$

$$C_p = C_v + R$$

$$(i) \quad \boxed{C_p - C_v = R} \quad \text{Mayer's formula}$$

$$(ii) \quad \boxed{\frac{C_p}{C_v} = \gamma}, \quad \gamma = \text{Poisson's ratio}$$

**5.10 WORK DONE IN DIFFERENT PROCESS :**

Here  $P_{2(g)}$  = Pressure of gas outside piston.

$P_{(g)}$  = Pressure of gas inside piston.

**(a) Work done in reversible isothermal process :**

$$P_{\text{external}} = \text{Variable}$$

For reversible process

$$P_{\text{ext}} = P_{\text{gas}} \pm dP$$

$$\therefore w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{ext.}} dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} (P_{\text{gas}} \pm dP) dV$$

Both  $dP$  and  $dV$  are very small so,  $(dP \cdot dV)$  is negligible.

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{gas}} dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$



$$w_{\text{rev.}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{\text{rev.}} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$\text{or, } \boxed{w_{\text{rev.}} = -2.303nRT \log_{10} \left( \frac{V_2}{V_1} \right)} \quad \dots(i)$$

according to Boyle's law at constant temperature  $P \propto \frac{1}{V}$  or  $PV = \text{constant}$

$$\therefore P_1 V_1 = P_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{w_{\text{rev.}} = -2.303nRT \log \left( \frac{P_1}{P_2} \right)} \quad \dots(ii)$$

**(b) Work done in reversible adiabatic process :**

In adiabatic process  $q = 0$

**FLOT** :  $\Delta E = q + w$

$$\Rightarrow \boxed{w = \Delta E} \Rightarrow w = nC_v \Delta T$$

$$\boxed{w = nC_v (T_2 - T_1)} \quad \dots\dots(i)$$

$$\therefore C_p - C_v = R$$

$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$$

$$\gamma - 1 = \frac{R}{C_v} \quad \left( \because \gamma = \frac{C_p}{C_v} \right) \Rightarrow C_v = \frac{R}{\gamma - 1} \quad \dots\dots\dots(ii)$$

From equation (i) and (ii)  $\boxed{w = \frac{nR}{\gamma - 1} (T_2 - T_1)} = \boxed{w = \frac{P_2 V_2 - P_1 V_1}{(\gamma - 1)}}$

**State equations of reversible adiabatic processes are :**

$$PV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$





## GOLDEN KEY POINTS

- Work in closed vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because  $P_{\text{ext}}$  is zero.
- Work in a chemical reaction  $w = -P\Delta V = -\Delta n_g RT$

## Illustrations

**Illustration 15** 5 moles of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat capacity of oxygen at constant pressure,

$$C_p = 7.03 \frac{\text{Cal}}{\text{molK}} \text{ and } R = 2 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

**Solution** We know mayer's relation is  $C_p - C_v = R$

$$C_v = C_p - R = 7.03 - 2 = 5.03 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

$$\text{As we know } \Delta E = nC_v dT = 5 \times 5.03 \times 10 = 251.5 \text{ Cal}$$

**Illustration 16** At 27°C, one mole of an ideal gas compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate  $\Delta E$  and  $q$  in calorie.

**Solution** For isothermal process  $\Delta E = 0$  and  $w = -2.303 nRT \log_{10} \frac{P_1}{P_2}$

$$w = -2.303 \times 1 \times 2 \times 300 \times \log \frac{2}{10}$$

$$w = + 2.303 \times 600 \times \log 5$$

$$w = + 2.303 \times 600 \times 0.699$$

$$w = + 965.87 \text{ Cal}$$

$$\text{For isothermal process} \quad \therefore w = -q$$

$$\therefore q = -965.87 \text{ Cal}$$

**Illustration 17** A gas expands from 3 dm<sup>3</sup> to 5 dm<sup>3</sup> against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water (if specific heat of water is 4.184 Jg<sup>-1</sup>K<sup>-1</sup>)

**Solution** Since work is done against constant  $P$  and thus, irreversible

$$\Delta V = 5 - 3 = 2 \text{ dm}^3 = 2 \text{ L}, P = 3 \text{ atm}$$

$$w = -P\Delta V = -3 \times 2 \text{ L atm} = -6 \times 101.3 \text{ J} = -607.8 \text{ Joule}$$

Now this work is used up in heating water

$$w = n \times C \times \Delta T$$

$$607.8 = 10 \times (4.184 \times 18) \times \Delta T$$

$$\Delta T = 0.81 = T_2 - T_1$$

$$\therefore \text{Final temperature} = T_1 + \Delta T = 290 + 0.81 = 290.81 \text{ K}$$



**Illustration 18** A sample of 3 mol of an ideal gas at 200K and 2 atm is compressed reversibly and adiabatically until the temperature reaches 250K, given that molar heat capacity is  $27.5 \text{ J K}^{-1} \text{ mol}^{-1}$  at constant volume, calculate  $w$ .

**Solution**  $C_v = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$

During reversible adiabatic process

$$w = nC_v (T_2 - T_1) = 3 \times 27.5 \times 50 = 4125 \text{ Joule}$$

**Illustration 19** 10 moles of an ideal gas at  $27^\circ\text{C}$  and 10 atm., pressure occupying a volume of 24.6 L undergoes the following changes.

- (i) Isothermal & reversible expansion to 246 L
- (ii) Isothermal and irreversible expansion to 246 L.
- (iii) Isochoric heating to  $177^\circ\text{C}$ .

Calculate the work done in each transformation in kJ.

**Solution** (i) Work done in isothermal reversible expansion

$$w = -2.303 \times nRT \log \frac{V_2}{V_1} = -2.303 \times 10 \times 8.31 \times 300 \times \log \frac{246}{24.6}$$

$$= -57413.79 \text{ J} = -57.41 \text{ kJ}$$

(ii) Work done in isothermal irreversible expansion

$$w = -P (V_2 - V_1) = -1 (246 - 24.6) = -221.4 \text{ L-atm} = -221.4 \times 101.3 \text{ J} = -22.43 \text{ kJ}$$

(iii) Work done in isochoric change

$$\text{Since } \Delta V = 0 \quad \therefore w = 0$$

**Illustration 20** Find the work done when 2 mol of a gas expands isothermally from  $5\text{dm}^3$  to  $40\text{dm}^3$  against a constant external pressure of 2 atm at 298K. Also calculate  $w_{\text{rev}}$  for the change.

**Solution** (i)  $w = -P\Delta V$

$$w = -2 \times (40 - 5)$$

$$w = -70 \ell \text{ atm} = -70 \times 101.3 \text{ J}$$

$$w = -7091 \text{ J}$$

(ii)  $w = -2.303 nRT \log \frac{V_2}{V_1}$

$$w = -2.303 \times 2 \times 8.314 \times 298 \log \frac{40}{5}$$

$$w = -10.3 \times 10^3 \text{ J}$$

#### BEGINNER'S BOX-4

- Calculate  $w$  for the isothermal reversible expansion of 1mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K :-  
 (1)  $-5227.2 \text{ J}$                       (2)  $+5227.2 \text{ J}$                       (3)  $-2257 \text{ J}$                       (4)  $+2257 \text{ J}$
- When 229 J of energy is supplied as heat at constant pressure to 3 mol Ar(g), the temperature of the sample is increased by  $2.55\text{K}$ . Calculate the molar heat capacity at constant volume :-  
 (1)  $30 \text{ kJ K}^{-1} \text{ mol}^{-1}$                       (2)  $30 \text{ J K}^{-1} \text{ mol}^{-1}$                       (3)  $21.7 \text{ J K}^{-1} \text{ mol}^{-1}$                       (4)  $21.7 \text{ kJ K}^{-1} \text{ mol}^{-1}$



## 5.11 SPONTANEOUS PROCESS AND NON-SPONTANEOUS PROCESS :

### (i) Spontaneous process :

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions.
- All natural processes are ir-reversible and spontaneous processes. The natural processes take place of their own in one direction only.

### (ii) Non-spontaneous process :

- The process which does not occur of its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

### Examples of spontaneous process that need no initiation :

**Ex.1** Flow of water from high level to low level.

Flow of heat from hot body to cold body.

Flow of charge from high potential to low potential.

Flow of gas from high pressure to low pressure.

**Ex.2** Melting of ice at 25° C

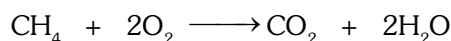
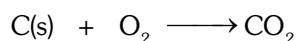
Evapouration of water at 25° C

Dissolution of common salt in water.

**Ex.3** Mixing of different non reacting gases

### Examples of spontaneous process that need initiation :

**Ex.1** Burning of fuel (coal, petrol)



**Ex.2** Lighting of candle

### Criteria for a process to be spontaneous :

- (i) Tendency to attain minimum energy or maximum stability (Energy Factor).
- (ii) Tendency to attain maximum randomness (Entropy Factor)

## 5.12 ENTROPY (S) :

- (i) The thermodynamic quantity, which is used to measure **degree of randomness** or **disorderness** of the system is called as entropy.  
Entropy (s)  $\propto$  Randomness or disorderness
- (ii) More is the disorderness, higher is the entropy.
- (iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Where  $q_{\text{rev}}$  = heat absorbed by the system in a reversible manner at the temperature T

**Unit :** J K<sup>-1</sup> or Cal K<sup>-1</sup>



(iv)  $\Delta S = S_{\text{final}} - S_{\text{initial}}$

If  $S_{\text{final}} > S_{\text{initial}}$  : Then  $\Delta S = \text{positive}$

If  $S_{\text{final}} < S_{\text{initial}}$  : Then  $\Delta S = \text{negative}$

(v) Entropy is an extensive property and state function.

(vi) Entropy change in a chemical reaction

$$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

(vii) Entropy change for a process :  $\Delta S = \frac{q_{\text{rev}}}{T}$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\text{or } \Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

**Case I** : For an ideal gas reversible isothermal process; :  $T_2 = T_1$

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

$$\Delta S = 2.303nR \log \frac{V_2}{V_1} = 2.303nR \log \frac{P_1}{P_2}$$

**Case II** : For an isochoric process  $V_2 = V_1$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} ; \quad \Delta S = 2.303 nC_v \log \frac{T_2}{T_1}$$

(viii) **For reversible adiabatic process :**

Entropy remains constant so process is also known as **isoentropic process**.

**Factors affecting entropy of system :**

(I) If  $\Delta n_g > 0$  then  $\Delta S > 0$

If  $\Delta n_g < 0$  then  $\Delta S < 0$

(II) Physical state :  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

**Ex.**  $\text{Fe(s)} \rightarrow \text{Fe(s)}$  :  $\Delta S = \text{positive}$   
           300K    400K

(V) On decreasing pressure, S increases.

**Ex.**  $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{g})$  :  $\Delta S = \text{positive}$   
           5atm    2 atm

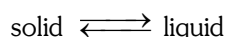
(VI) Mixture :  $\left. \begin{array}{l} \text{Solid} + \text{solid} \\ \text{liquid} + \text{liquid} \\ \text{gas} + \text{gas} \end{array} \right\} S \uparrow$



### Entropy change during phase transition :

#### (I) Entropy of fusion $[(\Delta S)_f]$ mole :

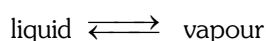
The entropy change, when 1 mol solid changes into liquid at its melting point temperature.



$$(\Delta S)_f = \frac{\Delta H_{\text{fusion}}}{T}$$

#### (II) Entropy of vapourisation $[(\Delta S)_{\text{vap}}]$ mole :

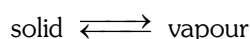
The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.



$$(\Delta S)_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

#### (III) Entropy of sublimation $[(\Delta S)_{\text{sub}}]$ mole :

The entropy change, when 1 mol solid changes into vapour at a particular temperature.



$$(\Delta S)_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

### Some famous or extra ordinary examples of entropy change :

(i) Entropy of graphite > Entropy of diamond.

(ii) In rusting of iron entropy increases.

(iii)  $\text{NH}_4\text{Cl(s)} + \text{aq} \longrightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

In this process  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions are free to move in solution where as they are not free to move in solid  $\text{NH}_4\text{Cl}$ . Hence  $\Delta S$  is positive for this type of dissolution process.

(iv) On addition of HCl in the aqueous solution of  $\text{Ag}^+$  ions entropy decreases due to precipitation of AgCl.

(v) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(vi) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

### Total entropy change in reversible process :

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other.

Let a system, releases  $q$  heat to the surroundings at temperature  $T$ .

$$\Delta S_{\text{system}} = \frac{-q}{T}; \quad \Delta S_{\text{surroundings}} = \frac{+q}{T}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{total}} = \frac{-q}{T} + \frac{q}{T} \Rightarrow \boxed{\Delta S_{\text{total}} = 0}$$



**Total entropy change in irreversible process :**

Let a system is at high temperature  $T_1$  and surroundings are at low temperature  $T_2$ .

Let  $q$  amount of heat is released by the system.

$$\Delta S_{\text{system}} = \frac{-q}{T_1}, \quad \Delta S_{\text{surroundings}} = \frac{+q}{T_2}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{-q}{T_1} + \frac{q}{T_2}$$

$$\therefore \boxed{\Delta S_{\text{total}} = +ve} \quad (\because T_1 > T_2)$$

Total entropy change for irreversible spontaneous process is always greater than zero.

**Spontaneity of a process in terms of total entropy change :**

If,  $\Delta S_{\text{total}} = +ve \Rightarrow$  spontaneous process

If,  $\Delta S_{\text{total}} = -ve \Rightarrow$  non spontaneous process

If,  $\Delta S_{\text{total}} = 0 \Rightarrow$  process is at equilibrium

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## Illustrations

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**Illustration 21** The enthalpy change for transition of liquid water to steam is  $40.8 \text{ kJ mol}^{-1}$  at  $373\text{K}$ . Calculate  $\Delta S$  for the process.

**Solution** The entropy change for the vapourization of water is given by  $\Delta S = \frac{\Delta H_{\text{vap.}}}{T}$

Given  $\Delta H_{\text{vap.}} = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 1000 \text{ J mol}^{-1}$  and  $T = 373 \text{ K}$

$$\Delta S = \frac{40.8 \times 1000 \text{ J mol}^{-1}}{373\text{K}} = 109.38 \text{ JK}^{-1} \text{ mol}^{-1}$$

**Illustration 22** Calculate the change in entropy for the fusion of  $1 \text{ mol}$  of ice. The melting point of ice is  $273\text{K}$  and molar enthalpy of fusion of ice =  $6 \text{ kJ mol}^{-1}$

**Solution**  $\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.97 \text{ JK}^{-1} \text{ mol}^{-1}$

**Illustration 23** The enthalpy of vapourisation of liquid diethyl ether  $(\text{C}_2\text{H}_5)_2\text{O}$ , is  $26.0 \text{ kJ mol}^{-1}$  at its boiling point ( $35.0^\circ\text{C}$ ). Calculate  $\Delta S$  for conversion of :-

(i) Liquid to vapour and (ii) Vapour to liquid at  $35^\circ\text{C}$

**Solution** (i)  $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{308} = 84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

(ii)  $\Delta S_{\text{cond.}} = \frac{\Delta H_{\text{cond.}}}{T} = \frac{-26 \times 10^3}{308} = -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$



**Illustration 24** Which of the following processes are accompanied by increase of entropy :

- (i) Dissolution of iodine in a solvent [ $I_2(s) \longrightarrow I_2(aq.)$ ]
- (ii) HCl is added to  $AgNO_3$  and a precipitate of AgCl is obtained.
- (iii) A partition is removed to allow two gases to mix.

**Solution** Increase of entropy : (i) and (iii)

### BEGINNER'S BOX-5

1. In any natural process, occurring in the universe :-
  - (1) Entropy is conserved
  - (2) Entropy increases
  - (3) Entropy decreases
  - (4) Entropy remains unchanged
2. The most random state of  $H_2O$  system is :-
  - (1) Ice
  - (2)  $H_2O(l)$  at  $80^\circ C$  ; 1 atm
  - (3) Steam
  - (4)  $H_2O(l)$  at  $25^\circ C$  ; 1 atm
3. Change in entropy is negative for :-
  - (1)  $Br_2(l) \longrightarrow Br_2(g)$
  - (2)  $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$
  - (3)  $M_2(g, 10 \text{ atm}) \longrightarrow M_2(g, 1 \text{ atm})$
  - (4)  $Fe \text{ (at } 400K) \longrightarrow Fe \text{ (at } 300K)$
4. Entropy change in spontaneous adiabatic process is :-
  - (1) Zero
  - (2)  $< 0$
  - (3)  $> 0$
  - (4) None of these
5. 5 mole of an ideal gas expand reversibly from a volume of  $8 \text{ dm}^3$  to  $80 \text{ dm}^3$  at a temperature of  $27^\circ C$ . The change in entropy is :-
  - (1)  $41.57 \text{ JK}^{-1}$
  - (2)  $-95.73 \text{ JK}^{-1}$
  - (3)  $95.73 \text{ JK}^{-1}$
  - (4)  $-41.57 \text{ JK}^{-1}$
6. The latent heat of vapourisation of water at  $100^\circ C$  is  $540 \text{ Cal g}^{-1}$ . Calculate the entropy increase when one mole of water at  $100^\circ C$  is evaporated :-
  - (1)  $26 \text{ Cal K}^{-1} \text{ mol}^{-1}$
  - (2)  $1.45 \text{ Cal K}^{-1} \text{ mol}^{-1}$
  - (3)  $367 \text{ Cal K}^{-1} \text{ mol}^{-1}$
  - (4)  $1.82 \text{ Cal K}^{-1} \text{ mol}^{-1}$
7. Calculate enthalpy of vapourization per mole of ethanol. Given  $\Delta S = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and B.P. of ethanol is  $78.5^\circ C$  :-
  - (1) Zero
  - (2)  $38.594 \text{ kJ mol}^{-1}$
  - (3)  $3.85 \text{ kJ mol}^{-1}$
  - (4) None of these

### 5.13 SECOND LAW OF THERMODYNAMICS (SLOT) :

- (i) It states about the direction of flow of heat
- (ii) All natural processes in universe are ir-reversible process or natural processes are spontaneous process.
- (iii) Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

$$(\Delta S)_T = +ve \quad \text{or} \quad (\Delta S)_T > 0 \quad \text{or} \quad (\Delta S)_{\text{system}} + (\Delta S)_{\text{surr.}} > 0$$



### 5.14 GIBB'S ENERGY (G or F) :

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.
- The term Gibbs energy was introduced to explain criteria of spontaneity in terms of system.
  - Since ; energy = useful work + randomness energy

$$H = G + TS$$

$$\boxed{G = H - TS} \quad \dots(i)$$

So the function that takes both enthalpy and entropy of system into account is called Gibbs energy.

- Gibbs energy is an extensive property and state function.
- Absolute value of G can't be measured but change can be measured, So we discuss ( $\Delta G$ )

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

From eq. (i)  $\boxed{\Delta G = \Delta H - T\Delta S}$

Where  $\Delta G$  = Change in Gibb's energy

$\Delta H$  = Change in enthalpy

$\Delta S$  = Change in entropy

#### Relation between Gibb's energy change and non expansion work or useful work :

$$\text{FLOT : } \Delta E = q + W$$

If, work is done by the system, then,  $\Delta E = q - W \quad \dots(i)$

According to Gibb's, system does both expansion and non expansion work.

$$\therefore W = W_{\text{expansion}} + W_{\text{non expansion}}$$

$$W = P\Delta V + W_{\text{non expansion}}$$

Put W in equation (i)

$$\Rightarrow \Delta E = q - (P\Delta V + W_{\text{non expansion}})$$

$$q = \Delta E + P\Delta V + W_{\text{non expansion}}$$

$$q = \Delta H + W_{\text{non expansion}} \quad (\because \Delta H = \Delta E + P\Delta V)$$

$$T\Delta S = \Delta H + W_{\text{non expansion}} \quad (\because \Delta S = q/T)$$

$$W_{\text{non expansion}} = T.\Delta S - \Delta H \quad (\because \Delta G = \Delta H - T\Delta S)$$

$$\Rightarrow \boxed{W_{\text{non expansion}} = -\Delta G} \text{ or } \boxed{W_{\text{useful}} = -\Delta G}$$

The decrease in Gibb's energy of system is equal to the non expansion work or useful work.

#### Relation in between $\Delta G$ of system and $\Delta S_{\text{total}}$ or Gibb's energy change and spontaneity :

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Let system releases heat at constant temperature T and pressure P.

$$\therefore q = q_p = \Delta H$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$





$$\Rightarrow \Delta H_{\text{system}} = -\Delta H_{\text{surroundings}}$$

$$\Delta S_{\text{surr.}} = \frac{\Delta H_{\text{surr.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys.}}}{T}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \left( \frac{-\Delta H_{\text{sys.}}}{T} \right)$$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys.}} - \Delta H_{\text{sys.}}$$

$$T\Delta S_{\text{total}} = -(\Delta H_{\text{sys.}} - T\Delta S_{\text{sys.}})$$

$$T\Delta S_{\text{total}} = -\Delta G_{\text{sys.}}$$

or  $\Delta G_{\text{sys.}} = -T\Delta S_{\text{total}}$

- (i) If,  $\Delta S_{\text{total}} = +ve \Rightarrow \Delta G_{\text{system}} = -ve \Rightarrow$  spontaneous process  
 (ii) If,  $\Delta S_{\text{total}} = -ve \Rightarrow \Delta G_{\text{system}} = +ve \Rightarrow$  non spontaneous process  
 (iii) If,  $\Delta S_{\text{total}} = 0 \Rightarrow \Delta G_{\text{system}} = 0 \Rightarrow$  process is at equilibrium.

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description
-	+	-	Reaction spontaneous at all temperature
-	-	-	(at low T) Reaction spontaneous at low temperature
-	-	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	-	(at high T) Reaction spontaneous at high temperature
+	-	+	(at all T) Reaction nonspontaneous at all temperatures

### Relationship between standard Gibbs energy change ( $\Delta G^\circ$ ) and Equilibrium constant ( $K_{\text{eq}}$ ) :-

For a reaction  $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium -  $\Delta G = 0$  and  $Q = K_{\text{eq}}$

$$0 = \Delta G^\circ + RT \ln K_{\text{eq}}$$

$$\therefore \Delta G^\circ = -RT \ln K_{\text{eq}} \quad \dots(i)$$

$$\text{or } \Delta G^\circ = -2.303RT \log_{10} K_{\text{eq}} \quad \dots(ii)$$

from equation (i)

$$\log K_{\text{eq}} = -\frac{\Delta G^\circ}{RT}$$

$$\therefore K_{\text{eq}} = e^{-\Delta G^\circ/RT} \quad \dots(iii)$$



## Illustrations

**Illustration 25.** For a certain reaction the change in enthalpy and change in entropy are  $40.63 \text{ kJ mol}^{-1}$  and  $100 \text{ JK}^{-1}$ . What is the value of  $\Delta G$  at  $27^\circ\text{C}$  and indicate whether the reaction is possible or not ?

**Solution** We know that :

$$\Delta G = \Delta H - T\Delta S$$

$$T = 27 + 273 = 300\text{K}$$

$$\Delta H = 40.63 \times 10^3 \text{ J mol}^{-1} = 40630 \text{ J mol}^{-1}$$

$$\Delta S = 100 \text{ JK}^{-1}$$

$$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = + 10630 \text{ J}$$

Positive value of  $\Delta G$  indicates that the reaction is not possible.

**Illustration 26** For a reaction at  $25^\circ\text{C}$  enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) are  $-11.7 \times 10^3 \text{ J mol}^{-1}$  and  $-105 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively. Find out whether this reaction is spontaneous or not.

**Solution**  $\Delta G = \Delta H - T\Delta S$

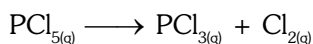
$$= -11700 - 298 \times (-105)$$

$$= +19590 \text{ J}$$

$\Delta G = +ve$ , so reaction is non-spontaneous.

**Illustration 27** Calculate the equilibrium constant for the reaction given below at  $400\text{K}$ .

If  $\Delta H^\circ = 77.2 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$



**Solution**  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 77200 - 400 \times 122 = 28400 \text{ J}$

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$\text{or } 28400 = -2.303 \times 8.31 \times 400 \log K_c$$

$$\text{or } K_c = 1.958 \times 10^{-4}$$

**Illustration 28** For the reaction,  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$ ;  $\Delta H = -95.4 \text{ kJ}$  and  $\Delta S = -198.3 \text{ J K}^{-1}$ . Calculate the temperature at which the reaction will proceed in forward direction.

**Solution**  $\Delta G = \Delta H - T\Delta S$

$\therefore$  At equilibrium  $\Delta G = 0$

$$\therefore \Delta H = T\Delta S \quad \text{so } T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ J K}^{-1}} = 481 \text{ K}$$

For this reaction  $\Delta H$  is  $-ve$  and  $\Delta S$  is  $-ve$ , so it will be spontaneous at low temperature.

$\therefore$  Below  $481\text{K}$  the reaction would be spontaneous.



**Illustration 29** Enthalpy and entropy changes of a reaction are  $40.63 \text{ kJ mol}^{-1}$  and  $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. Analyse the feasibility of the reaction at  $27^\circ\text{C}$ .

**Solution**  $\Delta H = 40.63 \text{ kJ mol}^{-1} = 40630 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$   
Now  $\Delta G = \Delta H - T\Delta S$   
 $= 40630 \text{ J mol}^{-1} - (300 \text{ K}) \times (108.8 \text{ J K}^{-1} \text{ mol}^{-1})$   
 $\Delta G = 7990 \text{ J mol}^{-1}$ .

Since  $\Delta G$  is positive, the reaction is not feasible in the forward direction.

**Illustration 30** For a certain reaction the change in enthalpy and change in entropy are  $40.63 \text{ kJ mol}^{-1}$  and  $100 \text{ JK}^{-1}$ . Show that the reaction at  $27^\circ\text{C}$  is possible or not.

**Solution**  $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = 40.63 - 300 \times 100 \times 10^{-3}$   
 $\Delta G = + 10.630 \text{ kJ}$   
 $\Delta G$  is positive so reaction is not possible.

**Illustration 31** Zinc reacts with dilute hydrochloric acid to give hydrogen at  $17^\circ\text{C}$ . The enthalpy of the reaction is  $-12.55 \text{ kJ mol}^{-1}$  and entropy change is  $5 \text{ JK}^{-1} \text{ mol}^{-1}$  for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

**Solution** Given  $\Delta H = -12.55 \text{ kJ mol}^{-1}$  and  $\Delta S = 5 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $T = 17 + 273 = 290 \text{ K}$   
Applying  $\Delta G = \Delta H - T \Delta S$

$$\begin{aligned} &= -12.55 \frac{\text{kJ}}{\text{mol}} - 290\text{K} \times \frac{5}{1000} \frac{\text{kJ}}{\text{Kmol}} \\ &= -12.55 - 1.45 \\ &= -14 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Since  $\Delta G$  is negative, the reaction will be spontaneous

**Illustration 32** For a reaction both  $\Delta H$  and  $\Delta S$  are positive under what condition will the reaction occur spontaneously.

**Solution** The reaction will occur spontaneously only when  $T\Delta S > \Delta H$ .

$$\Delta G = \Delta H - T\Delta S = (+) - T(+)$$

For  $\Delta G$  to be negative,  $T\Delta S$  must be  $> \Delta H$

**Illustration 33** Which of the following are state function ?

(i)  $q$                       (ii) Entropy                      (iii) Specific heat capacity                      (iv)  $H$                       (v)  $w$

**Solution** **Ans.** (ii), (iii) and (iv)



**BEGINNER'S BOX-6**

1. If  $\Delta G^\circ > 0$  for a reaction then :-  
(1)  $K_p > 1$                       (2)  $K_p < 1$                       (3)  $K_p = 1$                       (4) None
2. For an endothermic reaction to be spontaneous :-  
(1)  $\Delta G$  must be +ve                      (2)  $\Delta S$  must be  $> 0$   
(3)  $T\Delta S$  must be -ve                      (4)  $T\Delta S$  must be equal to  $\Delta G$
3. The value of  $\Delta G$  for the process  $\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$  at 1 atm and 260 K is :-  
(1)  $< 0$                       (2)  $= 0$                       (3)  $> 0$                       (4) Unpredictable
4. In a certain chemical reaction  $\Delta H = 150 \text{ KJ}$  and  $\Delta S = 10 \text{ JK}^{-1}$  at 300 K. The value of  $\Delta G$  would be :-  
(1)  $-2850 \text{ J}$                       (2) Zero  
(3)  $+2850 \text{ J}$                       (4)  $147 \text{ kJ}$
5. The standard Gibb's energy change for a gaseous reaction at  $27^\circ\text{C}$  is  $X \text{ kCal}$ . If equilibrium constant for a reaction is 100 and  $R$  is  $2 \text{ Cal K}^{-1} \text{ mol}^{-1}$ . Then  $X$  is :-  
(1)  $-2.7636$                       (2)  $+2.7636$                       (3)  $+ 807$                       (4)  $- 807$
6. The favourable conditions for a spontaneous reaction are :-  
(1)  $T\Delta S > \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = +ve$                       (2)  $T\Delta S > \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = -ve$   
(3)  $T\Delta S = \Delta H$ ,  $\Delta H = -ve$ ,  $\Delta S = -ve$                       (4)  $T\Delta S = \Delta H$ ,  $\Delta H = +ve$ ,  $\Delta S = +ve$

**5.15 THIRD LAW OF THERMODYNAMICS (TLOT)**

At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

**Exceptions :**

- (i)  $\text{NO}$ ,  $\text{N}_2\text{O}$                       (ii)  $\text{CO}$ ,  $\text{CO}_2$                       (iii) Mixture of isotopes                      (iv) Ice



# ENERGETICS

## 5.16 INTRODUCTION :

**Thermochemistry** is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

In this chapter we will introduced enthalpies of some specific reaction. Like, Enthalpy of formation ( $\Delta H_f$ ), Enthalpy of combustion ( $\Delta H_{\text{comb}}$ ), Bond dissociation enthalpy ( $\Delta H_{\text{BDE}}$ ) & Enthalpy of Neutralisation ( $\Delta H_{\text{neutralization}}$ )

### THERMOCHEMICAL REACTION :

The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermo chemical reaction.



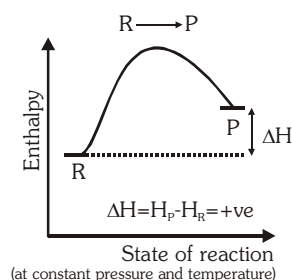
**Thermo chemical reaction are of 2 types.**

#### (i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.

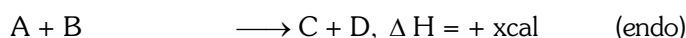
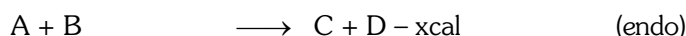
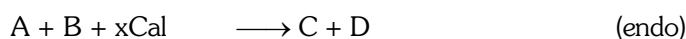
$$\Delta H = +ve$$

$$\Delta H = H_P - H_R = +ve \text{ i.e. } H_P > H_R$$



- (a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.
- (b) The product formed in the endothermic reaction is called endothermic compound.
- (c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

#### Representation of endothermic reaction :



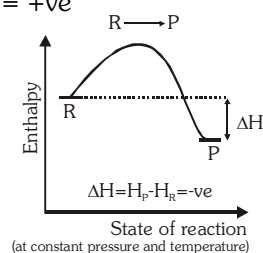
#### Examples :

- (I) Dissociation reactions (mostly)
- (II) Fusion reactions
- (III) Vaporization reactions
- (IV) Sublimation reactions
- (V) Photosynthesis  $6\text{CO}_2 + 6\text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ ,  $\Delta H = +ve$

#### (ii) Exothermic reaction :

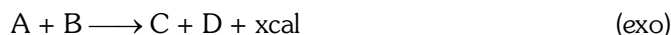
The reaction which evolves heat is called as exothermic reaction.

$$\Delta H = -ve \quad \Delta H = H_P - H_R = -ve \text{ i.e. } H_P < H_R$$



- (a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.  
 (b) The product formed in the exothermic reaction is called exothermic compound.  
 (c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

### Representation of exothermic reaction.

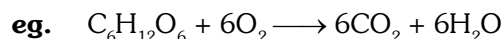


### Examples :

(I) Combustion reactions

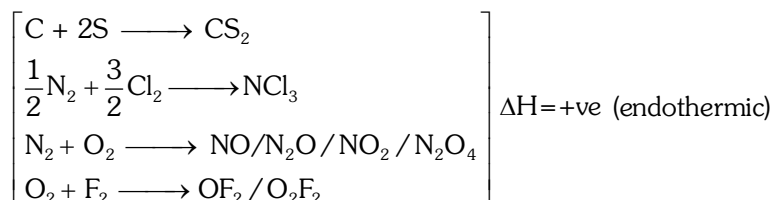
(II) Neutralisation reactions

(III) Respiration reaction



(IV) Formation reaction  $\begin{matrix} \nearrow \text{endo} \\ \searrow \text{exo (generally)} \end{matrix}$

Exceptions of formation reaction :



## GOLDEN KEY POINTS

- (i) If conditions are not given then,  $\Delta H$  is considered to be  $\Delta H^\circ$ .  
 (ii) If thermochemical reaction is multiplied by a coefficient then,  $\Delta H$  of reaction is also multiplied by that coefficient.  
 e.g.  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -285 \text{ kJ mol}^{-1}$   
 $2\text{H}_2(\text{g}) + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}(\ell) \quad \Delta H = -2 \times 285 \text{ kJ}$   
 (iii) If reaction is reversed then numerical value of  $\Delta H$  remains same but sign is changed.  
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -285 \text{ kJ mol}^{-1}$   
 $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = +285 \text{ kJ mol}^{-1}$

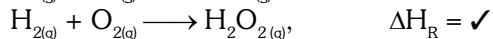
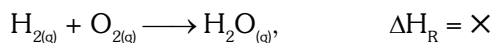
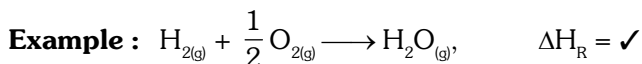
## BEGINNER'S BOX-7

- An endothermic reaction is one in which :  
 (1) heat is converted into electricity  
 (2) heat is absorbed  
 (3) heat is evolved  
 (4) heat is converted into mechanical work
- If heat of reaction  $A + 5B \longrightarrow 2C + 3D$ , is  $-50 \text{ kJ}$ . What is the heat of the reaction  $2A + 10B \longrightarrow 4C + 6D$ .  
 (1)  $-50 \text{ kJ}$  (2)  $-25 \text{ kJ}$  (3)  $-100 \text{ kJ}$  (4)  $+100 \text{ kJ}$
- The process  $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$ , should be :  
 (1) exothermic (2) endothermic  
 (3) neither exothermic nor endothermic (4) exothermic or endothermic depending upon temperature
- For the given reaction :  
 $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) ; \Delta H = 40 \text{ kJ}$   
 The  $\Delta H$  is specifically called  
 (1) Heat of formation of CO (2) Heat of combustion  
 (3) Heat of reaction (4) Heat of hydrogenation of C = O bond



### 5.17 HEAT OF REACTION OR (ENTHALPY OF REACTION) OR ( $\Delta H_R$ ) :

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.



**Note :** Heat of reaction at constant pressure is  $\Delta H$  and heat of reaction at constant volume is  $\Delta E$ .

#### Factors affecting heat of reaction :

##### (i) Reaction condition :

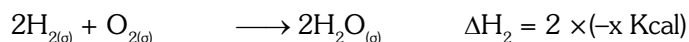
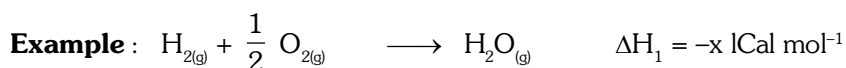
- (a) The chemical reactions are carried out at constant temperature with either pressure or volume constant.

At constant pressure  $q_p = \Delta H_{\text{reaction}}$

At constant volume  $q_v = \Delta E_{\text{reaction}}$

$$\Delta H = \Delta E + \Delta n_g RT$$

##### (ii) Quantity of reactant :



If equation is multiplied by coefficient then value of  $\Delta H$  is also multiplied by that coefficient.

##### (iii) Physical state of products and reactants :



If the physical state of product is different then the value of  $\Delta H$  is different.

**Note :** For  $\text{H}_2\text{O}$  (liq.),  $\Delta H$  is more negative in comparison to the formation of  $\text{H}_2\text{O}$  (vap.) because when vapours convert into liquid then some heat is released.

##### (iv) Allotropic form : (Physical nature of reactant)



##### (v) Temperature :

Effect of temperature on heat of reaction is given by **Kirchoff equation**

(i) at constant pressure :  $\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{Pm}$

$$\Delta C_{Pm} = \Sigma(C_{Pm/P}) - \Sigma(C_{Pm/R})$$

$\Delta H_{T_1}$  = Heat of reaction at  $T_1$  temperature

$\Delta H_{T_2}$  = Heat of reaction at  $T_2$  temperature

(ii) at constant volume :  $\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}$

$$\Delta C_{Vm} = \Sigma(C_{Vm/P}) - \Sigma(C_{Vm/R})$$

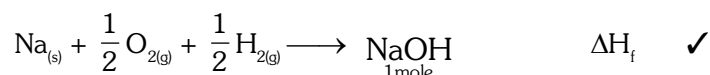
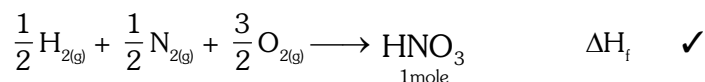
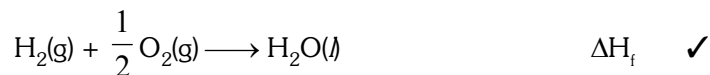


## 5.18 TYPES OF HEAT OF REACTION :

### (A) Heat of formation, Enthalpy of formation ( $\Delta H_f$ ) or ( $\Delta_f H$ ) :

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are  $O_2$  gas,  $C_{\text{graphite}}$  and  $S_{\text{rhombic}}$ , respectively some reactions with standard molar enthalpies of formation are :



### APPLICATION OF $\Delta H_f$ :

#### Calculation of $\Delta H$ of any general reaction.

Let us considered a general reaction  $aA + bB \rightarrow cC + dD$

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{f(\text{products})} - \Sigma \Delta H_{f(\text{reactant})} = [c\Delta H_{f(C)} + d\Delta H_{f(D)}] - [a\Delta H_{f(A)} + b\Delta H_{f(B)}]$$

### GOLDEN KEY POINTS

- Standard condition means,  $P = 1 \text{ atm}$ ,  $T = 25^\circ\text{C}$  or  $298 \text{ K}$   
Standard heat of formation is represent by  $\Delta H_f^\circ$ .
- If no condition is given then value of  $\Delta H_f$  is considered as  $\Delta H_f^\circ$ .
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	Reference state
C	$C_{(\text{graphite})}$
S	$S_{8(\text{Rhombic})}$ (Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(\text{white})}$
O	$O_{2(g)}$
H	$H_{2(g)}$
Br	$Br_{2(l)}$
Metal	$M_{(s)}$ [except $Hg_{(l)}$ ]

- The formation reaction may be exothermic or endothermic.

## Illustrations

**Illustration 34** Since enthalpy of elements in their natural state is taken as zero. The value of  $\Delta H_f$  of compounds :

- |                                 |                        |
|---------------------------------|------------------------|
| (1) is always negative          | (2) is always positive |
| (3) may be positive or negative | (4) is zero            |

**Solution** **Ans. (3)**

**Illustration 35** The enthalpy of formation of ammonia at  $298\text{K}$  is given as  $\Delta H_f^\circ = -46.11 \text{ kJ per mol of } NH_3(g)$ . To which of the following equation does this value apply ?

- |   |   |
|---|---|
| (1) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$ | (2) $N(g) + 3H(g) \longrightarrow NH_3(g)$                            |
| (3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$                       | (4) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(l)$ |

**Solution** **Ans. (1)**





**Illustration 36** Which of the following equation represents the standard heat of formation :

- (1)  $\text{C(diamond)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$  (2)  $\text{C(graphite)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$   
 (3)  $\text{C(diamond)} + 4\text{H}(\text{g}) \longrightarrow \text{CH}_4(\text{g})$  (4)  $\text{C(graphite)} + 4\text{H}(\text{g}) \longrightarrow \text{CH}_4(\text{g})$

**Solution** **Ans. (2)**

**Illustration 37** Which of the following reaction defines  $\Delta H_f^\circ$

- (1)  $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  (2)  $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{HF}(\text{g})$   
 (3)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$  (4)  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

**Solution** **Ans. (2)**

**Illustration 38** How much heat will be required at constant pressure to form 1.28 kg of  $\text{CaC}_2$  from  $\text{CaO}(\text{s})$  &  $\text{C}(\text{s})$ ?

Given :  $\Delta_f H^\circ (\text{CaO}, \text{s}) = -152 \text{ kCal mol}^{-1}$

$\Delta_f H^\circ (\text{CaC}_2, \text{s}) = -14 \text{ kCal mol}^{-1}$

$\Delta_f H^\circ (\text{CO}, \text{g}) = -26 \text{ kCal mol}^{-1}$

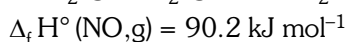
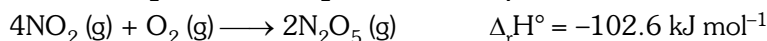
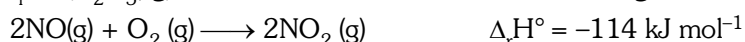
- (1) + 112 kCal (2) 224 kCal (3) 3840 kCal (4) 2240 kCal

**Solution.**  $\text{CaO}(\text{s}) + 3\text{C}(\text{s}) \longrightarrow \text{CaC}_2(\text{s}) + \text{CO}(\text{g})$

$$\Delta_f H^\circ = (-14 - 26) - (-152) = +112 \text{ kCal mol}^{-1}$$

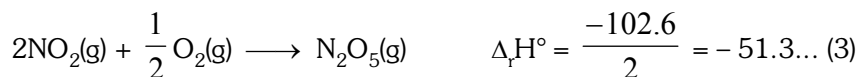
$$\text{Total heat required} = \left( \frac{1280}{64} \right) \times 112 \Rightarrow 2240 \text{ kCal}$$

**Illustration 39** The  $\Delta_f H^\circ (\text{N}_2\text{O}_5, \text{g})$  in  $\text{kJ mol}^{-1}$  on the bases of the following data is :

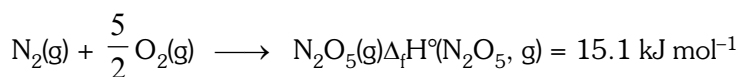


- (1) 15.1 (2) 30.2 (3) -36.2 (4) none of these

**Solution**  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) \quad \Delta_f H^\circ = 90.2$



From Equations (1) + (2) + (3)

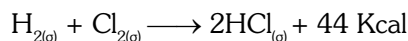


**Illustration 40** Calculate  $\Delta H^\circ$  for  $2\text{Al}_{(\text{s})} + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{Fe}_{(\text{s})} + \text{Al}_2\text{O}_3$  given that standard enthalpy of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  are  $-196.5$  and  $-399.1 \text{ kCal}$ .

**Solution**  $\Delta H_{\text{Reaction}}^0 = \Sigma \Delta H_{\text{P}}^0 - \Sigma \Delta H_{\text{R}}^0$   
 $= [2 \times \Delta H_{\text{Fe}(\text{s})}^0 + \Delta H_{\text{Al}_2\text{O}_3}^0] - [2 \times \Delta H_{\text{Al}(\text{s})}^0 + \Delta H_{\text{Fe}_2\text{O}_3}^0] = 2 \times 0 + (-399.1) - [2 \times 0 + (-196.5)]$   
 $\Delta H_{\text{Reaction}}^0 = -202.6 \text{ kCal}$



**Illustration 41** The heat of formation of the compound in the following reaction is :



- (1)  $-44 \text{ kCal mol}^{-1}$       (2)  $-22 \text{ kCal mol}^{-1}$       (3)  $+11 \text{ kCal mol}^{-1}$       (4)  $-88 \text{ kCal mol}^{-1}$

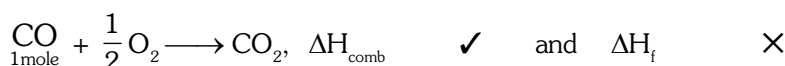
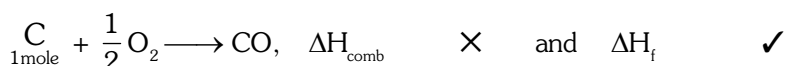
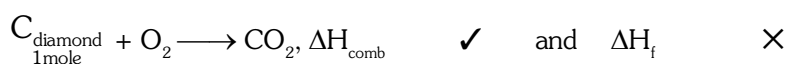
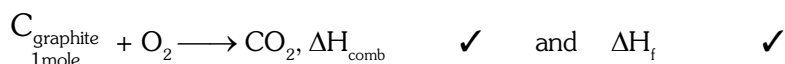
**Solution**      **Ans. (2)**

For the formation of 1 mol of HCl from elements  $\Delta H_f^\circ = -\frac{44}{2} = -22 \text{ Kcal}$

**(B) Heat of combustion ( $\Delta H_{\text{comb}}$ ) :**

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

**Example :**



**Note :**

- (I) Heat of combustion reaction is always exothermic
- (II) If conditions are not given then  $\Delta H_{\text{comb}}$  considered as  $\Delta H_{\text{comb}}^\circ$ .
- (III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\Delta H = \Sigma (\Delta H_{\text{comb}})_R - \Delta (\Delta H_{\text{comb}})_P$$

**APPLICATION OF HEAT OF COMBUSTION :**

**Calorific value or fuel value (C.V.) :**

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\text{Calorific value} = \frac{\Delta H_{\text{comb}}}{\text{Molecular weight}}$$

**Unit :-**  $\text{kJ g}^{-1}$  or  $\text{kCal g}^{-1}$

**GOLDEN KEY POINTS**

- Heat of combustion reaction is always exothermic
- If conditions are not given then  $\Delta H_{\text{comb}}$  is considered as  $\Delta H_{\text{comb}}^\circ$ .
- Maximum value of calorific value = Maximum efficiency or best fuel
- $\text{H}_2$  has the highest calorific value ( $150 \text{ kJ/g}$ ) but it is not used as domestic or industrial fuel due to some technical problems.

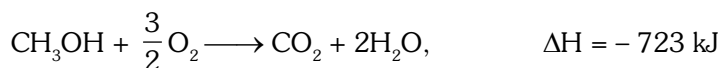


## Illustrations

**Illustration 42** 1 mole of methanol, when burnt in oxygen, gives out  $-723 \text{ kJ mol}^{-1}$  heat. If 1 mole of oxygen is used what will be the amount of heat evolved?

- (1) 723 kJ                      (2) 964 kJ                      (3) 482 kJ                      (4) 241 kJ

**Solution** **Ans. (3)**



with 1 mole of  $\text{O}_2$ ,  $\Delta H = -\frac{2}{3} \times 723 = -482 \text{ kJ}$

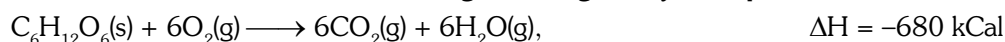
**Illustration 43** Combustion of methane :

- (1) is an exothermic reaction                      (2) is an endothermic reaction  
(3) requires a catalyst                      (4) gives  $\text{H}_2$

**Solution** **Ans. (1)**

Combustion is always exothermic

**Illustration 44** The heat evolved in the combustion of glucose is given by the equation



The wt. of  $\text{CO}_2(\text{g})$  produced when 170 kCal of heat is evolved in the combustion of glucose is

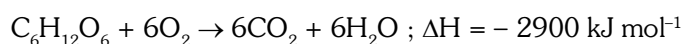
- (1) 264 g                      (2) 66 g                      (3) 11 g                      (4) 44 g

**Solution** **Ans. (2)**

Evolution of 680 Kcal is accompanied by  $\text{CO}_2 = 6 \times 44 = 264 \text{ g}$

Evolution of 170 Kcal is accompanied by  $\text{CO}_2 = \frac{264}{680} \times 170 = 66 \text{ g}$

**Illustration 45** Find out the calorific value of Glucose



**Solution**  $\therefore$  Heat evolved from 1 mol glucose = 2900 kJ

or Heat evolved from 180 gram glucose = 2900 kJ

$\therefore$  Heat evolved from 1 gram glucose =  $\frac{2900}{180} = 16.11 \text{ kJ g}$

or another method  $\text{C.V.} = \frac{\Delta H_{\text{comb}}}{M_w} = \frac{2900}{180} = 16.11 \text{ kJ g}$

**Illustration 46** Enthalpy of combustion of a substance is always :

- (1)  $> 0$                       (2)  $\geq 0$                       (3)  $\leq 0$                       (4)  $< 0$

**Solution** **Ans. (4)**

**Illustration 47** The heat change for a reaction :  $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2(\text{g})$  refers to

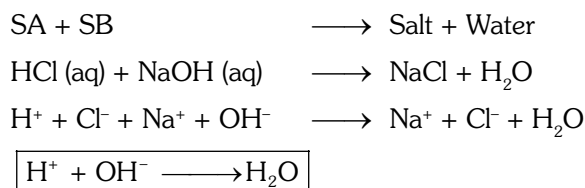
- (1) enthalpy of formation of carbon dioxide                      (2) enthalpy of combustion of carbon dioxide  
(3) enthalpy of vapourisation                      (4) enthalpy of combustion of carbon monoxide

**Solution** **Ans. (4)**

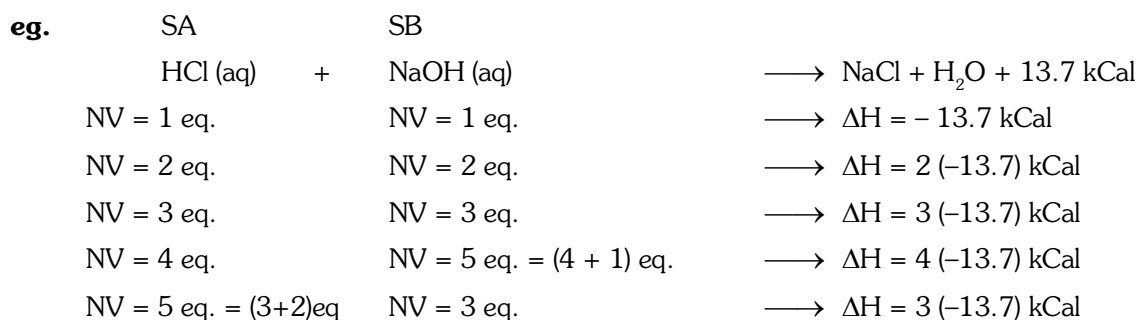


**(C) Heat of neutralisation ( $\Delta H_{\text{neut}}$ ) :**

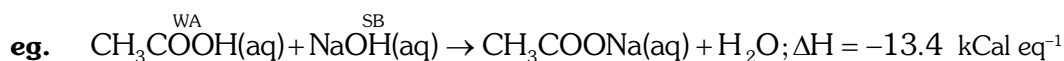
The heat evolved when one equivalent of an acid is completely neutralised by one equivalent of a base in dilute solution is called as heat of neutralisation.

**Note :**

- (i) When one equivalent of SA is neutralised by one equivalent of SB then evolve heat remain constant and its value is  $-13.7 \text{ kCal/equivalent}$  or  $-57.2 \text{ kJ equivalent}^{-1}$ .



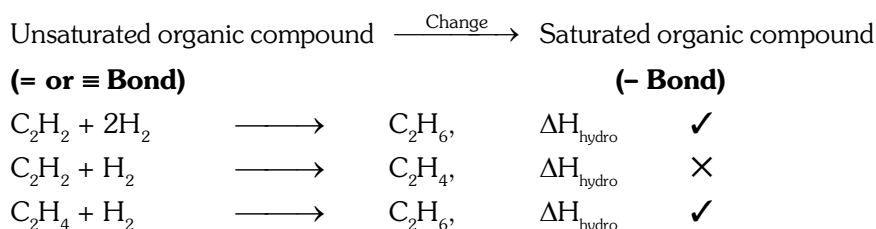
- (ii) If one of the acid or base or both are weak then heat of neutralization is usually less than  $-13.7 \text{ KCal eq}^{-1}$  or  $-57.3 \text{ kJ eq}^{-1}$  because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

**Exception :**

For a reaction  $\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}; \Delta H = -16.7 \text{ Kcal}$ ; this is because of hydration of  $\text{F}^-$  ion.

**(D) Heat of hydrogenation ( $\Delta H_{\text{Hydrogenation}}$ ) :**

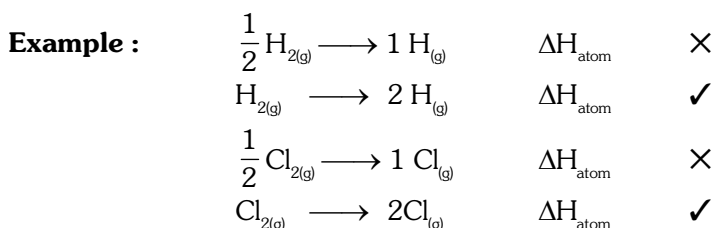
The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.



**Note :** Heat of hydrogenation is exothermic process.

**(E) Heat of atomization ( $\Delta H_{\text{atom}}$ ) :**

The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.

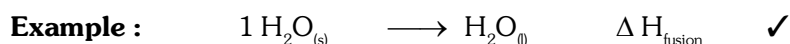


**Note :** It is an endothermic reaction.



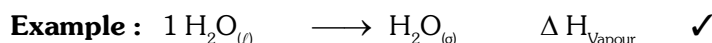
## (F) HEAT OF TRANSFORMATION :

- (i) **Heat of fusion ( $\Delta H_{\text{fusion}}$ )**: The required amount of heat to convert 1 mole solid into liquid at its melting point is called as heat of fusion.



**Note :** Heat of fusion is always endothermic reaction i.e. ( $\Delta H = +ve$ )

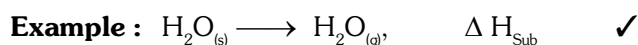
- (ii) **Heat of vapourization ( $\Delta H_{\text{vapour}}$ )**: The required amount of heat to convert 1 mole liquid into gas at its boiling point is called as heat of vapourization.



**Note :** Heat of vapourization is always endothermic reaction i.e. ( $\Delta H = +ve$ )

- (iii) **Heat of sublimation ( $\Delta H_{\text{sub}}$ )** :

The required amount of heat to convert 1 mole solid into gas at a certain temperature is called as heat of sublimation.



**Note :** Heat of sublimation is always endothermic reaction i.e. ( $\Delta H = +ve$ )

## Illustrations

**Illustration 48** Heat of neutralisation of an acid by a base is maximum when :

- (1) Both the acid and base are weak
- (2) Both the acid and base are strong
- (3) The acid is strong and the base is weak
- (4) The acid is weak and the base is strong

**Solution**

**Ans. (2)**

Heat of neutralisation is maximum ( $57.2 \text{ kJ eq}^{-1}$  or  $13.7 \text{ kCal eq}^{-1}$ ) when both acid and base are strong.

**Illustration 49** The enthalpy change for the process  $\text{C}_{(s)} \longrightarrow \text{C}_{(g)}$  corresponds to the enthalpy of

- (1) fusion
- (2) vapourization
- (3) combustion
- (4) sublimation

**Solution**

**Ans. (4)**

Solid  $\longrightarrow$  gas, is sublimation.

**Illustration 50** If  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + 13.7 \text{ kCal}$ , then heat of complete neutralisation of 1 gm mol of  $\text{H}_2\text{SO}_4$  with base in excess will be :

- (1)  $-13.7 \text{ kCal}$
- (2)  $-27.4 \text{ kCal}$
- (3)  $-6.85 \text{ kCal}$
- (4)  $-3.425 \text{ kCal}$

**Solution**

**Ans. (2)**

Moles of  $\text{H}_2\text{SO}_4 = 1 \text{ mol}$

g eq. of  $\text{H}_2\text{SO}_4 = \text{moles} \times \text{V.F.} = 1 \times 2 = 2 \text{ g eq.}$

Heat evolve due to 2 g eq. =  $-13.7 \times 2 = -27.4 \text{ kCal}$

**Illustration 51**  $200 \text{ cm}^3$  of  $0.1 \text{ M H}_2\text{SO}_4$  is mixed with  $150 \text{ cm}^3$  of  $0.2 \text{ M KOH}$ . Find the value of evolved heat.

**Solution**

$\text{H}_2\text{SO}_4$

$\text{KOH}$

eq. =  $\text{NV} = (0.1 \times 2) \times 0.2$

$(0.2 \times 1) \times (0.15)$

= 0.04

= 0.03

Heat liberated by 1 eq. =  $57.2 \text{ kJ}$

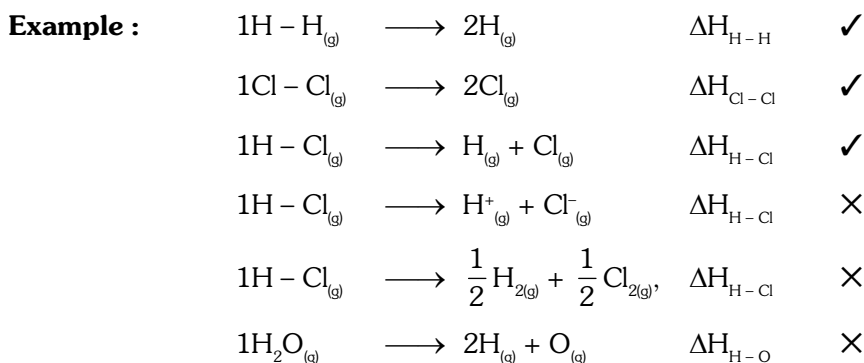
So heat liberated by 0.03 eq. =  $57.2 \times 0.03 = 1.7 \text{ kJ}$



## BEGINNER'S BOX-8

## (I) Bond energy / Bond dissociation energy :

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy**.



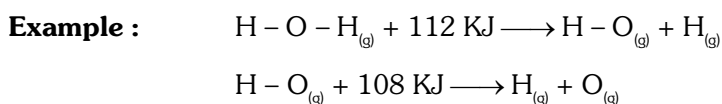
### GOLDEN KEY POINTS

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then  $\Delta H$  of that reaction can be calculate as follows.

$$\Delta H = \Sigma (\text{B.E.})_{\text{R}} - \Sigma (\text{B.E.})_{\text{P}}$$

- In the case of poly atomic molecule** we calculate the average bond energy.

$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}$$



$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{112 + 108}{2} = 110 \text{ kJ mol}^{-1}$$

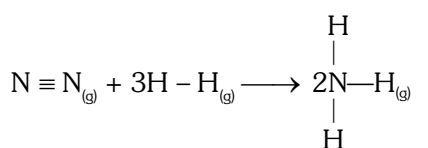
## Illustrations

**Illustration 52** Given the bond energy of  $\text{N} \equiv \text{N}$ ,  $\text{H} - \text{H}$  and  $\text{N} - \text{H}$  bonds are  $945$ ,  $436$  and  $391 \text{ kJ mol}^{-1}$  respectively, the enthalpy of the reaction  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \longrightarrow 2\text{NH}_{3(\text{g})}$  is :

(1)  $-93 \text{ kJ}$                       (2)  $102 \text{ kJ}$                       (3)  $90 \text{ kJ}$                       (4)  $105 \text{ kJ}$

**Solution**

**Ans. (1)**



$$\begin{array}{ll} 945 + 3 \times 436 & 2 \times (3 \times 391) \\ = 2253 \text{ kJ} & = 2346 \text{ kJ} \end{array}$$

$$\Delta H = \Sigma (\text{B.E.})_{\text{R}} - \Sigma (\text{B.E.})_{\text{P}} = 2253 - 2346 = -93 \text{ kJ}$$



**Illustration 53** The enthalpy changes at 298 K in successive breaking of O – H bonds of H – O – H are  

$$\text{H}_2\text{O}_{(g)} \longrightarrow \text{H}_{(g)} + \text{OH}_{(g)}, \quad \Delta H = 498 \text{ kJ mol}^{-1}$$

$$\text{OH}_{(g)} \longrightarrow \text{H}_{(g)} + \text{O}_{(g)}, \quad \Delta H = 428 \text{ kJ mol}^{-1}$$
The bond enthalpy of the O – H bond is  
(1) 498 kJ mol<sup>-1</sup>      (2) 463 kJ mol<sup>-1</sup>      (3) 428 kJ mol<sup>-1</sup>      (4) 70 kJ mol<sup>-1</sup>

**Solution** **Ans. (2)**

$$(\text{B.E.})_{\text{av}} = \frac{498 + 428}{2} = 463 \text{ kJ}$$

**Illustration 54** The required heat for dissociation of 1 mol H<sub>2</sub>O into its atoms (H and oxygen) is ΔH<sub>Dis.</sub>. Then calculate the bond energy of O – H bond.

**Solution**  $\text{H}_2\text{O}_{(g)} \rightarrow \text{O}_{(g)} + 2\text{H}_{(g)}; \Delta H_{\text{Dissociation}}$   
 $\text{H} - \text{O} - \text{H}_{(g)} \longrightarrow \text{O}_{(g)} + 2\text{H}_{(g)}; \Delta H_{\text{Dissociation}}$   
 $\therefore$  required energy for breaking the 2 mol O – H bond = ΔH<sub>Dis.</sub>  
 $\therefore$  required energy for 1 mole =  $\frac{\Delta H_{\text{Dis.}}}{2}$ ;  $\Delta H_{\text{O-H}} = \frac{\Delta H_{\text{Dis.}}}{2}$

**Illustration 55** Calculate the bond energy of C – H Bond in methane.

**Solution**  $\text{CH}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{H}_{(g)}; \Delta H_{\text{Dis.}}$   
or 
$$\begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{H}_{(g)} \\ | \\ \text{H} \end{array} \longrightarrow \text{C}_{(g)} + 4\text{H}_{(g)}; \Delta H_{\text{Dis.}}$$
  
 $\therefore$  Bond energy of 4 mol C – H = ΔH<sub>Dis.</sub>  
 $\therefore$  Bond energy of 1 mol C – H bond =  $\frac{\Delta H_{\text{Dis.}}}{4}$

**Illustration 56** The energy change of reaction  $\text{C}_2\text{H}_{6(g)} \longrightarrow 2\text{C}_{(g)} + 6\text{H}_{(g)}$  is X kJ. The bond energy of C – H bond is:

- (1)  $\frac{X}{6} \text{ kJ mol}^{-1}$       (2)  $\frac{X}{3} \text{ kJ mol}^{-1}$       (3) X kJ /mol<sup>-1</sup>      (4) unpredictable from data

**Solution** **Ans. (4)**

**Illustration 57**  $\text{CuSO}_4(\ell) + 5\text{H}_2\text{O}(\text{s}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}); \Delta H = -x \text{ kJ}$

The value of ΔH represents :

- (1) enthalpy of solution of copper (II) sulphate  
(2) enthalpy of hydration of copper (II) sulphate  
(3) enthalpy of hydrolysis of copper (II) sulphate  
(4) lattice energy of copper (II) sulphate

**Solution** **Ans. (2)**

**Illustration 58** The bond energy of hydrogen is 103 kCal mol<sup>-1</sup>. This means that :

- (1) 103 kCal are required to break  $6.023 \times 10^{23}$  gaseous H<sub>2</sub> molecules into gaseous atoms  
(2) 103 kCal are required to break the bonds in one gram of hydrogen  
(3) 103 kCal are required to break one bond to form two atoms of hydrogen  
(4) 103 kCal are required to break one mole of gaseous hydrogen molecules into ions.

**Solution** **Ans. (1)**

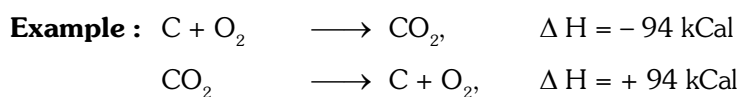




## 5.19 LAWS OF THERMOCHEMISTRY :

### (I) LAVOISIER AND LAPLACE LAW :

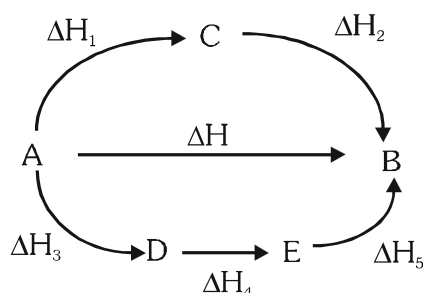
Enthalpy of formation of compound is **numerically equal** to the enthalpy of decomposition of that compound with **opposite sign**.



### (II) HESS LAW OF CONSTANT HEAT SUMMATION :

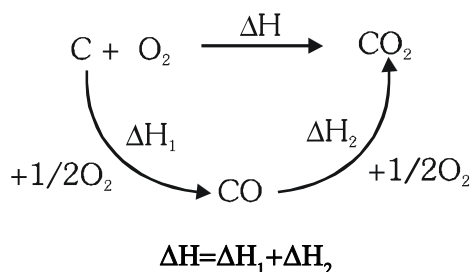
The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

**Example - 1 :**



$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 \\ \text{or} \quad \Delta H &= \Delta H_3 + \Delta H_4 + \Delta H_5 \\ \text{or} \quad \Delta H &= \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5\end{aligned}$$

**Example - 2 :**



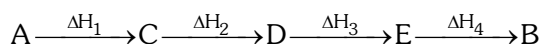
## GOLDEN KEY POINTS

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position**, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction**.

## Illustrations

**Illustration 59** Single step reaction  $\text{A} \rightarrow \text{B}$  ;  $\Delta H = ?$

Multi step reaction to produce B from A is given



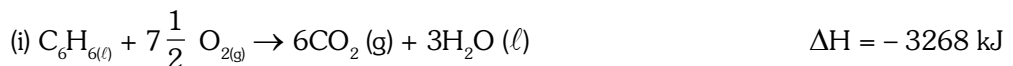
**Solution**

According to Hess's law  $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$



**Illustration 60** Calculate the heat of formation of Benzene. The reaction is given below :  
 $6\text{C(s)} + 3\text{H}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{6(\text{l})}$  and  $-3268$ ,  $-393.5$  and  $-285.8 \text{ kJ mol}^{-1}$  are the heats of combustion of benzene, heat of formation of  $\text{CO}_2$  and heat of formation of  $\text{H}_2\text{O}(\text{l})$  respectively.

**Solution** Target reaction  $6\text{C}_{(\text{s})} + 3\text{H}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{6(\text{l})}$   
 Given

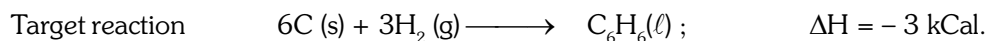
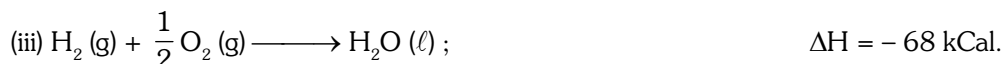
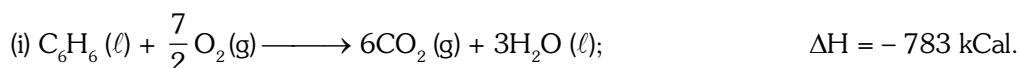


$$6 \times \text{eq. (ii)} + 3 \times \text{eq. (iii)} - \text{eq. (i)}$$

$$\Delta H = 6 \times -393.5 + 3 \times -285.8 - (-3268) = +49.6 \text{ kJ mol}^{-1}$$

**Illustration 61** The heats of formation of  $\text{CO}_{2(\text{g})}$  and  $\text{H}_2\text{O}_{(\text{l})}$  are  $-97$  and  $-68 \text{ kCal mol}^{-1}$ . The heat of combustion of benzene is  $-783 \text{ kCal mol}^{-1}$ . What will be the heat of formation of benzene ?

**Solution** Given :

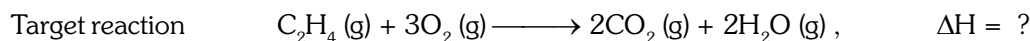
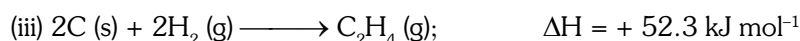
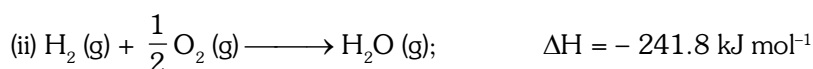
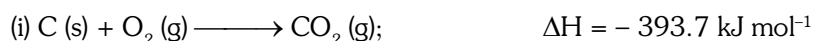


$$6 \times \text{eq. (ii)} + 3 \times \text{eq. (iii)} - \text{eq. (i)}$$

$$\Delta H = 6 \times -97 + 3 \times -68 - (-783) = -3 \text{ kCal mol}^{-1}$$

**Illustration 62** Calculate the enthalpy of combustion of ethylene (gas) to form  $\text{CO}_2$  (gas) and  $\text{H}_2\text{O}$  (gas) at  $298 \text{ K}$  and  $1$  atmospheric pressure. The enthalpies of formation of  $\text{CO}_{2(\text{g})}$ ,  $\text{H}_2\text{O}_{(\text{g})}$  and  $\text{C}_2\text{H}_{4(\text{g})}$  are  $-393.7$ ,  $-241.8$ ,  $+52.3 \text{ kJ per mol}$  respectively.

**Solution** We are given :



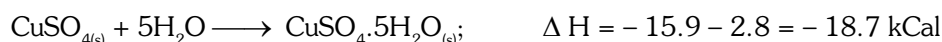
$2 \times \text{Equation (i)} + 2 \times \text{Equation (ii)} - \text{Equation (iii)}$  gives

$$\Delta H = 2(-393.7) + 2(-241.8) - (52.3) = -1323.3 \text{ kJ mol}^{-1}$$

**Illustration 63** The heat of solution of anhydrous  $\text{CuSO}_{4(\text{s})}$  is  $-15.9 \text{ kCal mol}^{-1}$  and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{s})}$  is  $2.8 \text{ kCal mol}^{-1}$ . Calculate the heat of hydration of  $\text{CuSO}_{4(\text{s})}$ .

**Solution** Given  $\text{CuSO}_{4(\text{s})} + \text{aq.} \longrightarrow \text{CuSO}_4(\text{aq}) \quad \Delta H = -15.9 \text{ kCal} \dots \text{(i)}$   
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{s})} + \text{aq.} \longrightarrow \text{CuSO}_4(\text{aq}) \quad \Delta H = +2.8 \text{ kCal} \dots \text{(ii)}$

Subtracting Eq. (ii) from Eq.(i)



Heat of hydration of  $\text{CuSO}_4 = -18.7 \text{ kCal mol}^{-1}$



## BEGINNER'S BOX-9

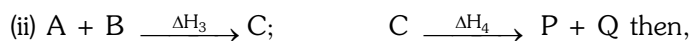
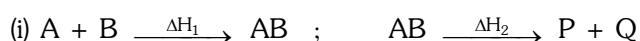
1. A hypothetical reaction,  $X \longrightarrow 2Y$  proceeds by the following sequence of steps



The value of  $\Delta H$  of reaction is :

- (1)  $q_1 + q_2 + q_3$       (2)  $2q_1 + 2q_2 + 3q_3$       (3)  $2(q_1 + q_2 + 2q_3)$       (4)  $2(q_1 + q_2 + q_3)$

2. Consider two paths of a certain reaction



(1)  $(\Delta H_1 + \Delta H_2) > (\Delta H_3 + \Delta H_4)$

(2)  $(\Delta H_1 + \Delta H_2) = (\Delta H_3 + \Delta H_4)$

(3)  $(\Delta H_2 + \Delta H_3) = (\Delta H_1 + \Delta H_4)$

(4)  $(\Delta H_1 + \Delta H_2) < (\Delta H_3 + \Delta H_4)$

## ANSWER KEY

<b>BEGINNER'S BOX-1</b>	<b>Que.</b>	1	2	3	4						
	<b>Ans.</b>	1	1	1	1						
<b>BEGINNER'S BOX-2</b>	<b>Que.</b>	1	2	3	4						
	<b>Ans.</b>	3	4	2	1						
<b>BEGINNER'S BOX-3</b>	<b>Que.</b>	1	2	3	4	5	6	7	8		
	<b>Ans.</b>	2	2	2	3	1	2	4	3		
<b>BEGINNER'S BOX-4</b>	<b>Que.</b>	1	2								
	<b>Ans.</b>	1	3								
<b>BEGINNER'S BOX-5</b>	<b>Que.</b>	1	2	3	4	5	6	7			
	<b>Ans.</b>	2	3	4	3	3	1	2			
<b>BEGINNER'S BOX-6</b>	<b>Que.</b>	1	2	3	4	5	6				
	<b>Ans.</b>	2	2	3	4	1	1				
<b>BEGINNER'S BOX-7</b>	<b>Que.</b>	1	2	3	4						
	<b>Ans.</b>	2	3	2	3						
<b>BEGINNER'S BOX-8</b>	<b>Que.</b>	1	2	3	4	5					
	<b>Ans.</b>	3	2	4	4	2					
<b>BEGINNER'S BOX-9</b>	<b>Que.</b>	1	2								
	<b>Ans.</b>	3	2								



## EXERCISE-I (Conceptual Questions)

### INTRODUCTION

- Thermodynamics is concerned with :-
  - (1) Total energy of a system
  - (2) Energy changes in a system
  - (3) Rate of a chemical change
  - (4) Mass changes in nuclear reactions
- A well stoppered thermos flask contains some ice cubes. This is an example of :-
  - (1) Closed system
  - (2) Open system
  - (3) Isolated system
  - (4) Non-thermodynamic system
- Identify the intensive quantity from the following -
  - (1) Enthalpy and temperature
  - (2) Volume and temperature
  - (3) Enthalpy and volume
  - (4) Temperature and refractive index
- Which of the following is an extensive property
  - (1) Mass
  - (2) Enthalpy
  - (3) Energy
  - (4) All of these
- For an adiabatic process which of the following relations is correct
  - (1)  $\Delta E = 0$
  - (2)  $P\Delta V = 0$
  - (3)  $q = 0$
  - (4)  $q = +W$
- In which of the following process work is independent of path :
  - (1) Isothermal
  - (2) Isochoric
  - (3) Adiabatic
  - (4) Isobaric
- When a gas is compressed adiabatically and reversibly, the final temperature is-
  - (1) Higher than the initial temperature
  - (2) Lower than the initial temperature
  - (3) The same as initial temperature
  - (4) Dependent upon the rate of compression
- Which one is dependent only on initial and final state ?
  - (1) Heat supplied at constant pressure
  - (2) Heat supplied at constant volume
  - (3) Enthalpy
  - (4) All of the above
- Out of boiling point (I), entropy (II), pH (III) and emf of a cell (IV), intensive properties are :
  - (1) I, III, IV
  - (2) I, II
  - (3) I, II, III
  - (4) All of these

- The work done by a weightless piston in causing an expansion  $\Delta V$  (at constant temperature), when the opposing pressure  $P$  is variable, is given by :
  - (1)  $W = - \int PdV$
  - (2)  $W = 0$
  - (3)  $W = -P\Delta V$
  - (4) None
- The work done by 100 calorie of heat in isothermal expansion of ideal gas is :-
  - (1) 418.4 J
  - (2) 4.184 J
  - (3) 41.84 J
  - (4) None
- Temperature and volume are not :-
  - (1) Extensive properties
  - (2) Intensive properties
  - (3) Intensive and extensive properties respectively
  - (4) Extensive and intensive properties respectively
- $q = -w$  is not true for :-
  - (1) Isothermal process
  - (2) Adiabatic process
  - (3) Cyclic process
  - (4) 1 and 3 both
- The temperature of an ideal gas increase in an -
  - (1) Adiabatic compression
  - (2) Adiabatic expansion
  - (3) Isothermal expansion
  - (4) Isothermal compression
- Enthalpy of 1 mole monoatomic ideal gas is equals to :-
  - (1)  $\frac{3}{2}RT$
  - (2)  $\frac{5}{2}RT$
  - (3)  $RT$
  - (4)  $2RT$
- Which statement is true for reversible process :-
  - (1) It takes place in single step
  - (2) Driving force is much greater than opposing force
  - (3) Work obtain is minimum
  - (4) None

### FIRST LAW OF THERMODYNAMICS ( $\Delta E = q + W$ )

- Both  $q$  &  $w$  are \_ \_ \_ \_ function :-
  - (1) State
  - (2) State, Path
  - (3) Path, State
  - (4) Path
- If work done by the system is 300 joule when 100 cal. heat is supplied to it. The change in internal energy during the process is :-
  - (1) - 200 Joule
  - (2) 400 Joule
  - (3) 720 Joule
  - (4) 120 Joule



19. A system has internal energy equal to  $E_1$ , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -  
 (1)  $(E_1 + 150)$  (2)  $(E_1 + 1050)$   
 (3)  $(E_1 - 150)$  (4) None of these
20. The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :  
 (1) 32 J (2) 40 J  
 (3) 48 J (4) -32 J
21. If a gas absorbs 100 J of heat and expands by  $500\text{cm}^3$  against a constant pressure of  $2 \times 10^5 \text{Nm}^{-2}$ , the change in internal energy is:-  
 (1) - 300 J (2) - 100 J  
 (3) + 100 J (4) None of these

**ENTHALPY  $[\Delta H = \Delta E + P\Delta V/\Delta H = \Delta E + \Delta n_g RT]$**

22. Internal energy change during a reversible isothermal expansion of an ideal gas is :-  
 (1) Always negative  
 (2) Always positive  
 (3) Zero  
 (4) May be positive or negative
23. Under which of the following conditions is the relation,  $\Delta H = \Delta E + P\Delta V$  valid for a system :-  
 (1) Constant pressure  
 (2) Constant temperature  
 (3) Constant temperature and pressure  
 (4) Constant temperature, pressure and composition
24. The difference between heats of reaction at constant pressure and constant volume for the reaction  $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$  in KJ is  
 (1) + 7.43 (2) +3.72  
 (3) - 7.43 (4) - 3.72
25. For a gaseous reaction,  
 $\text{A}(\text{g}) + 3\text{B}(\text{g}) \longrightarrow 3\text{C}(\text{g}) + 3\text{D}(\text{g})$   
 $\Delta E$  is 17 kCal at  $27^\circ\text{C}$  assuming  $R = 2 \text{Cal K}^{-1} \text{mol}^{-1}$ , the value of  $\Delta H$  for the above reaction is:  
 (1) 15.8 Kcal (2) 18.2 Kcal  
 (3) 20.0 Kcal (4) 16.4 Kcal
26. Which of the following statements is correct for the reaction  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  at constant temperature and pressure  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H < \Delta E$   
 (3)  $\Delta H > \Delta E$  (4) None of the above
27. For the reaction  $\text{Ag}_2\text{O}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$ , which one of the following is true :  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H = \frac{1}{2}\Delta E$   
 (3)  $\Delta H < \Delta E$  (4)  $\Delta H > \Delta E$
28. A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If  $\Delta H$  is the enthalpy change and  $\Delta E$  is the change in internal energy, then :-  
 (1)  $\Delta H > \Delta E$  (2)  $\Delta H < \Delta E$   
 (3)  $\Delta H = \Delta E$  (4) Not definite
29. For the gaseous reaction involving the complete combustion of isobutane -  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H > \Delta E$   
 (3)  $\Delta H = \Delta E = 0$  (4)  $\Delta H < \Delta E$
30. For the reversible isothermal expansion of one mole of an ideal gas at 300 K, from a volume of  $10 \text{dm}^3$  to  $20 \text{dm}^3$ ,  $\Delta H$  is -  
 (1) 1.73 kJ (2) -1.73 kJ  
 (3) 3.46 kJ (4) Zero
31. For  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  at  $977^\circ\text{C}$ ,  $\Delta H = 174 \text{KJ/mol}$  ; then  $\Delta E$  is :-  
 (1) 160 kJ (2) 163.6 kJ  
 (3) 186.4 kJ (4) 180 kJ
32. Heat of reaction for ,  $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  at constant V is  $-67.71 \text{Kcal}$  at  $17^\circ\text{C}$ . The heat of reaction at constant P at  $17^\circ\text{C}$  is :-  
 (1)  $-68.0 \text{kCal}$  (2)  $+ 68.0 \text{kCal}$   
 (3)  $- 67.42 \text{kCal}$  (4) None
33. The reaction :-  

$$\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2}\text{O}_{2(\text{g})} \rightarrow \text{N}_{2(\text{g})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$$
  
 was carried out in a bomb calorimeter. The heat released was  $743 \text{kJ mol}^{-1}$ . The value of  $\Delta H_{300\text{K}}$  for this reaction would be :-  
 (1)  $- 740.5 \text{kJ mol}^{-1}$  (2)  $- 741.75 \text{kJ mol}^{-1}$   
 (3)  $- 743.0 \text{kJ mol}^{-1}$  (4)  $- 744.25 \text{kJ mol}^{-1}$
34. The enthalpy of vaporisation of water at  $100^\circ\text{C}$  is  $40.63 \text{kJ mol}^{-1}$ . The value  $\Delta E$  for this process would be:-  
 (1)  $37.53 \text{kJ mol}^{-1}$  (2)  $39.08 \text{kJ mol}^{-1}$   
 (3)  $42.19 \text{kJ mol}^{-1}$  (4)  $43.73 \text{kJ mol}^{-1}$
35. For the system  $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$  :-  
 (1)  $\Delta H = \Delta E$  (2)  $\Delta H > \Delta E$   
 (3)  $\Delta E > \Delta H$  (4)  $\Delta H = 0$



36. For the reaction  $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$   
Which one of the statement is correct at constant T and P ?  
(1)  $\Delta H = \Delta E$   
(2)  $\Delta H < \Delta E$   
(3)  $\Delta H > \Delta E$   
(4)  $\Delta H$  is Independent of physical state of reactants
37. Which is true for the combustion of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) at  $25^\circ\text{C}$  :-  
(1)  $\Delta H > \Delta E$  (2)  $\Delta H < \Delta E$   
(3)  $\Delta H = \Delta E$  (4) None
38. For which change  $\Delta H \neq \Delta E$  :-  
(1)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$   
(2)  $\text{HCl (l)} + \text{NaOH (l)} \rightarrow \text{NaCl (s)} + \text{H}_2\text{O (l)}$   
(3)  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$   
(4)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$
39. The heat of combustion of ethanol determined in a bomb calorimeter is  $-670.48 \text{ kCal mole}^{-1}$  at  $27^\circ\text{C}$ . What is  $\Delta H$  at  $27^\circ\text{C}$  for the reaction :-  
(1)  $-335.24 \text{ kCal}$  (2)  $-671.08 \text{ kCal}$   
(3)  $-670.48 \text{ kCal}$  (4)  $+670.48 \text{ kCal}$
40. The difference in  $\Delta H$  and  $\Delta E$  for the combustion of methane at  $25^\circ\text{C}$  would be :-  
(1) Zero (2)  $2 \times 298 \times -2 \text{ Cals.}$   
(3)  $2 \times 298 \times -3 \text{ Cals.}$  (4)  $2 \times 25 \times -3 \text{ Cals.}$
41. For which of the following reactions  $\Delta H$  is less than  $\Delta E$  :-  
(1)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)} + 6\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$   
(2)  $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$   
(3)  $\text{N}_2\text{O}_4\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$   
(4)  $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$
42. For a reaction  $2\text{X(s)} + 2\text{Y(s)} \rightarrow 2\text{C(l)} + \text{D(g)}$   
The  $q_p$  at  $27^\circ\text{C}$  is  $-28 \text{ kCal mol}^{-1}$ .  
The  $q_v$  is -----  $\text{kCal mol}^{-1}$  :-  
(1)  $-27.4$  (2)  $+27.4$   
(3)  $-28.6$  (4)  $28.6$

#### WORK DONE IN DIFFERENT PROCESS

43. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at  $25^\circ\text{C}$  is :  
(1)  $-2.303 \times 8.31 \times 10^7 \times 298 \log 2$   
(2)  $-2.303 \times 0.0821 \times 298 \log 2$   
(3)  $-2.303 \times 0.0821 \times 298 \log 0.5$   
(4)  $-2.303 \times 2 \times 298 \log 2$

44. Two litre of  $\text{N}_2$  at  $0^\circ\text{C}$  and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming the gas to be ideal calculate work of expansion ?  
(1)  $-504.2 \text{ Joule}$  (2)  $-405.2 \text{ Joule}$   
(3)  $+810.4 \text{ Joule}$  (4)  $-810.4 \text{ Joule}$
45. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :-  
(1) Zero (2) 2 J  
(3) 4 J (4) 8 J
46. One mole of a gas occupying  $3\text{dm}^3$  expands against a constant external pressure of 1 atm to a volume of 13 lit. The workdone is :-  
(1)  $-10 \text{ atm dm}^3$  (2)  $-20 \text{ atm dm}^3$   
(3)  $-39 \text{ atm dm}^3$  (4)  $-48 \text{ atm dm}^3$

#### ENTROPY/SECOND LAW OF THERMODYNAMICS

47. For which reaction from the following,  $\Delta S$  will be maximum ?  
(1)  $\text{Ca(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CaO(s)}$   
(2)  $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$   
(3)  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2 \text{(g)}$   
(4)  $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$
48. An adiabatic reversible process is one in which :-  
(1) Temperature of the system does not change  
(2) The system is not closed to heat transfer  
(3) There is no entropy change  
(4) None of these
49. Entropy means  
(1) Disorderliness (2) Randomness  
(3) Orderliness (4) both 1 & 2
50.  $\Delta S$  for the reaction;  
 $\text{MgCO}_3\text{(s)} \rightarrow \text{MgO(s)} + \text{CO}_2\text{(g)}$  will be :  
(1) 0 (2) -ve (3) +ve (4)  $\infty$
51. Change in entropy is negative for  
(1) Bromine (l)  $\rightarrow$  Bromine (g)  
(2)  $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)}$   
(3)  $\text{N}_2\text{(g, 10 atm)} \rightarrow \text{N}_2 \text{(g, 1 atm)}$   
(4)  $\text{Fe(at 400 K)} \rightarrow \text{Fe(at 300 K)}$
52. In which reaction  $\Delta S$  is positive :-  
(1)  $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (s)}$   
(2)  $3\text{O}_2 \text{(g)} \rightarrow 2\text{O}_3 \text{(g)}$   
(3)  $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}$   
(4)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3 \text{(g)}$





53. When the egg is hard boiled, there is-  
 (1) Increase in disorder  
 (2) Decrease in disorder  
 (3) No change in disorder  
 (4)  $\Delta G$  is negative
54. If  $S^\circ$  for  $H_2$ ,  $Cl_2$  and  $HCl$  are 0.13, 0.22 and 0.19  $kJ K^{-1} mol^{-1}$  respectively. The total change in standard entropy for the reaction  $H_2 + Cl_2 \longrightarrow 2HCl$  is :  
 (1) 30  $JK^{-1} mol^{-1}$  (2) 40  $JK^{-1} mol^{-1}$   
 (3) 60  $JK^{-1} mol^{-1}$  (4) 20  $JK^{-1} mol^{-1}$
55. Which has the least entropy :  
 (1) Graphite (2) Diamond  
 (3)  $N_2(g)$  (4)  $N_2O(g)$
56. When two gases are mixed the entropy :-  
 (1) Remains constant (2) Decreases  
 (3) Increases (4) Becomes zero
57. The enthalpy of vaporization for water is 186.5  $kJ mol^{-1}$ , the entropy of its vaporization will be-  
 (1) 0.5  $kJ K^{-1} mol^{-1}$  (2) 1.0  $kJ K^{-1} mole^{-1}$   
 (3) 1.5  $kJ K^{-1} mole^{-1}$  (4) 2.0  $kJ K^{-1} mole^{-1}$
58. The enthalpy of vaporisation of per mole of ethanol (b.p. = 79.5°C and  $\Delta S = 109.8 JK^{-1} mol^{-1}$ ) is :-  
 (1) 27.35  $kJ mol^{-1}$  (2) 32.19  $kJ mol^{-1}$   
 (3) 38.70  $kJ mol^{-1}$  (4) 42.37  $kJ mol^{-1}$
59. If 900J/g of heat is exchanged at boiling point of water, then what is increase in entropy?  
 (1) 43.4  $JK^{-1}mole^{-1}$   
 (2) 87.2  $JK^{-1}mole^{-1}$   
 (3) 900  $JK^{-1}mole^{-1}$   
 (4) Zero
60. 5 mole of an ideal gas expand reversibly from a volume of 8  $dm^3$  to 80 $dm^3$  at a temperature of 27°C. The change in entropy is :-  
 (1) 41.57  $JK^{-1}$  (2) - 95.73  $JK^{-1}$   
 (3) 95.73  $JK^{-1}$  (4) - 41.57  $JK^{-1}$
61. In a spontaneous irreversible process the total entropy of the system and surroundings  
 (1) Remains constant (2) Increases  
 (3) Decreases (4) Zero
62. The total entropy change for a system & its surroundings increases if the process is :  
 (1) Reversible (2) Irreversible  
 (3) Exothermic (4) Endothermic
63. Calculate the entropy of  $Br_2(g)$  in the reaction  $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ ,  $\Delta S^\circ = 20.1 JK^{-1}$  given, entropy of  $H_2$  and  $HBr$  is 130.6 and 198.5  $J mol^{-1} K^{-1}$  :-  
 (1) 246.3  $JK^{-1}$  (2) 123.15  $JK^{-1}$   
 (3) 24.63  $JK^{-1}$  (4) 20  $JK^{-1}$
64. Ammonium chloride when dissolved in water leads to cooling sensation. The dissolution of  $NH_4Cl$  at constant temperature is accompanied by :-  
 (1) Increase in entropy  
 (2) Decrease in entropy  
 (3) No change in entropy  
 (4) No change in enthalpy
65. In which of the following case entropy decreases-  
 (1) Solid changing to liquid  
 (2) Expansion of a gas  
 (3) Crystals dissolve  
 (4) Polymerisation
66. Which of the following state function is not zero at standard state :-  
 (1) Enthalpy (2) Entropy  
 (3) Free energy (4) Work
67. Entropy of an adiabatic reversible process is:-  
 (1) Positive (2) Zero  
 (3) Negative (4) Constant

### GIBBS FREE ENERGY

68. A gas is allowed to expand under reversible adiabatic conditions then what is zero for such a process:-  
 (1)  $\Delta G = 0$  (2)  $\Delta T = 0$   
 (3)  $\Delta S = 0$  (4) None of these
69. For a reaction at 25°C enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) are  $-11.7 \times 10^3 J mol^{-1}$  and  $-105 J mol^{-1} K^{-1}$  respectively. The reaction is :  
 (1) Spontaneous  
 (2) Non spontaneous  
 (3) At equilibrium  
 (4) Can't say anything
70. The spontaneous nature of a reaction is impossible if :  
 (1)  $\Delta H$  is +ve,  $\Delta S$  is also +ve  
 (2)  $\Delta H$  is -ve;  $\Delta S$  is also -ve  
 (3)  $\Delta H$  is -ve ;  $\Delta S$  is +ve  
 (4)  $\Delta H$  is +ve;  $\Delta S$  is -ve
71. If  $\Delta H > 0$  and  $\Delta S > 0$ , the reaction proceeds spontaneously when :-  
 (1)  $\Delta H > 0$  (2)  $\Delta H < T \Delta S$   
 (3)  $\Delta H = T \Delta S$  (4) None



- 72.** The temperature at which the reaction  $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + \frac{1}{2}\text{O}_2\text{(g)}$  is at equilibrium is .....;  
Given  $\Delta H = 30.5 \text{ kJ mol}^{-1}$   
and  $\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$  :  
(1) 462.12 K (2) 362.12 K  
(3) 262.12 K (4) 562.12 K
- 73.** The enthalpy change for a given reaction at 298 K is  $-x \text{ cal mol}^{-1}$ . If the reaction occurs spontaneously at 298 K, the entropy change at that temperature  
(1) Can be negative but numerically larger than  $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$   
(2) Can be negative but numerically smaller than  $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$   
(3) Cannot be negative  
(4) Cannot be positive
- 74.** Which of the following is true for the reaction  $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$  at  $100^\circ\text{C}$  and 1 atmosphere  
(1)  $\Delta S = 0$  (2)  $\Delta H = 0$   
(3)  $\Delta H = \Delta E$  (4)  $\Delta H = T\Delta S$
- 75.** For the reaction  $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + \frac{1}{2} \text{O}_2\text{(g)}$  the value of  $\Delta H = 30.56 \text{ kJ mol}^{-1}$  and  $\Delta S = 66 \text{ JK}^{-1} \text{ mol}^{-1}$ . The temperature at which the free energy change for the reaction will be zero is :-  
(1) 373 K (2) 413 K  
(3) 463 K (4) 493 K
- 76.** For hypothetical reversible reaction  $\frac{1}{2}\text{A}_2\text{(g)} + \frac{3}{2}\text{B}_2\text{(g)} \longrightarrow \text{AB}_3\text{(g)}$ ;  $\Delta H = -20 \text{ kJ}$  if standard entropies of  $\text{A}_2$ ,  $\text{B}_2$  and  $\text{AB}_3$  are 60, 40 and  $50 \text{ JK}^{-1} \text{ mole}^{-1}$  respectively. The above reaction will be in equilibrium at :-  
(1) 400 K (2) 500 K  
(3) 250 K (4) 200 K
- 77.** For the precipitation of  $\text{AgCl}$  by  $\text{Ag}^+$  ions and  $\text{HCl}$   
(1)  $\Delta H = 0$  (2)  $\Delta G = 0$   
(3)  $\Delta G = -ve$  (4)  $\Delta H = \Delta G$
- 78.** What is the sign of  $\Delta G$  for the process of ice melting at  $283 \text{ K}$  ?  
(1)  $\Delta G > 0$  (2)  $\Delta G = 0$   
(3)  $\Delta G < 0$  (4) None of these
- 79.** What is the free energy change  $\Delta G$ , when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure :-  
(1) 540 Cal (2) -9800 Cal  
(3) 9800 Cal (4) 0 Cal
- 80.** A reaction  $\text{A} + \text{B} \longrightarrow \text{C} + \text{D} + q$  is found to have a positive entropy change, the reaction will be -  
(1) Possible at high temperature  
(2) Possible only at low temperature  
(3) Not possible at any temperature  
(4) Possible at any temperature
- 81.** Equilibrium constant of a reaction is related to :  
(1) Standard free energy change  $\Delta G^\circ$   
(2) Free energy change  $\Delta G$   
(3) Entropy change  
(4) None
- 82.** The Vant Hoff equation is :  
(1)  $\Delta G^\circ = RT \log_e K_p$  (2)  $-\Delta G^\circ = RT \log_e K_p$   
(3)  $\Delta G^\circ = RT^2 \ln K_p$  (4) None
- 83.** If  $\Delta G^\circ > 0$  for a reaction then :  
(1)  $K_p > 1$   
(2)  $K_p < 1$   
(3) The products predominate in the equilibrium mixture  
(4) None
- 84.** If the equilibrium constant for a reaction is 10, then the value of  $\Delta G^\circ$  will be  
( $R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $T = 300 \text{ K}$ )  
(1)  $+ 5.527 \text{ kJ mol}^{-1}$   
(2)  $- 5.527 \text{ kJ mol}^{-1}$   
(3)  $+55.27 \text{ kJ mol}^{-1}$   
(4)  $- 55.27 \text{ kJ mol}^{-1}$
- 85.** The process of evaporation of a liquid is accompanied by :  
(1) Increase in enthalpy  
(2) Decrease in free energy  
(3) Increase in entropy  
(4) All
- 86.** For the process,  $\text{CO}_2\text{(s)} \longrightarrow \text{CO}_2\text{(g)}$  :  
(1) Both  $\Delta H$  and  $\Delta S$  are +ve  
(2)  $\Delta H$  is negative and  $\Delta S$  is +ve  
(3)  $\Delta H$  is +ve and  $\Delta S$  is -ve  
(4) Both  $\Delta H$  and  $\Delta S$  are -ve
- 87.** Which of the following provide exceptions to third law of thermodynamics  
(1) CO (2) ice  
(3)  $\text{CO}_2$  (4) All the above
- 88.** The Gibbs free energy change of a reaction at  $27^\circ\text{C}$  is  $-26 \text{ kCal}$ . and its entropy change is  $-60 \text{ Cals K}$ .  $\Delta H$  for the reaction is :-  
(1)  $- 44 \text{ kCals}$ . (2)  $- 18 \text{ kCals}$ .  
(3)  $34 \text{ kals}$ . (4)  $- 24 \text{ kCals}$ .



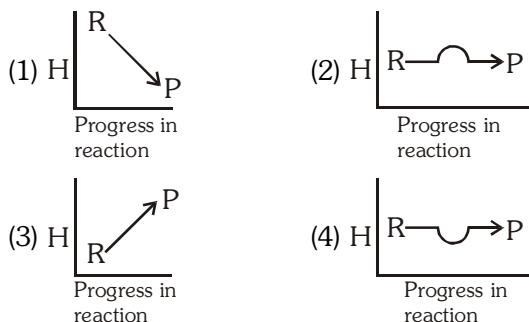


89. Which of the following reaction is expected never to be spontaneous :-
- (1)  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$   $\Delta H = -Ve$ ,  $\Delta S = +Ve$
  - (2)  $\text{Mg}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{MgH}_2$   $\Delta H = -Ve$ ,  $\Delta S = -Ve$
  - (3)  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$   $\Delta H = +Ve$ ,  $\Delta S = +Ve$
  - (4)  $2\text{Ag}(\text{s}) + 3\text{N}_2(\text{g}) \rightarrow 2\text{AgN}_3$   $\Delta H = +Ve$ ,  $\Delta S = -Ve$

### THERMOCHEMICAL REACTION

90. The formation of water from  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is an exothermic process because :
- (1) The chemical energy of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is more than that of water
  - (2) The chemical energy of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is less than that of water
  - (3) The temperature of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is higher than that of water
  - (4) The temperature of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is lower than that of water

91. Which plot represents for an exothermic reaction:



92. Which one of the following is not applicable for a thermochemical equation :
- (1) It tells about physical state of reactants and products
  - (2) It tells whether the reaction is spontaneous
  - (3) It tells whether the reaction is exothermic or endothermic
  - (4) It tells about the allotropic form (if any) of the reactants
93. The correct thermochemical equation is :
- (1)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$  ;  $\Delta H = -94 \text{ kCal}$
  - (2)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$  ;  $\Delta H = +94.0 \text{ kCal}$
  - (3)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  ;  $\Delta H = -94 \text{ kCal}$
  - (4)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  ;  $\Delta H = +94 \text{ kCal}$
94. The enthalpy changes of formation of the gaseous oxide of nitrogen ( $\text{N}_2\text{O}$  and  $\text{NO}$ ) are positive because of :
- (1) The high bond energy of the nitrogen molecule
  - (2) The high electron affinity of oxygen atoms
  - (3) The high electron affinity of nitrogen atoms
  - (4) The tendency of oxygen to form  $\text{O}^{2-}$

95.  $\Delta H$  for transition of carbon from diamond form to graphite form is  $-453.5 \text{ Cal}$ . This suggests that :
- (1) Graphite is chemically different from diamond
  - (2) Graphite is as stable as diamond
  - (3) Graphite is more stable than diamond
  - (4) Diamond is more stable than graphite

96. Which of the following values of heat of formation indicates that the product is least stable
- (1)  $-94 \text{ kCal}$
  - (2)  $-231.6 \text{ kCal}$
  - (3)  $+21.4 \text{ kCal}$
  - (4)  $+64.8 \text{ kCal}$

97. Heat of formation,  $\Delta H_f^\circ$  of an explosive compound like  $\text{NCl}_3$  is -
- (1) Positive
  - (2) Negative
  - (3) Zero
  - (4) Positive or negative

98. According to the following reaction  
 $\text{C}(\text{s}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$ ,  $\Delta H = -26.4 \text{ kCal}$
- (1) CO is an endothermic compound
  - (2) CO is an exothermic compound
  - (3) The reaction is endothermic
  - (4) None of the above

99. Which of the following represents an exothermic reaction:-
- (1)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ ,  $\Delta H = 180.5 \text{ kJ}$
  - (2)  $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$ ,  $\Delta E = 131.2 \text{ kJ}$
  - (3)  $2\text{HgO}(\text{s}) + 180.4 \text{ KJ} \rightarrow 2\text{Hg}(\text{l}) + \text{O}_2(\text{g})$
  - (4)  $2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s})$ ,  $\Delta E = -693.8 \text{ kJ}$

100. The heat change during the reaction  $24\text{g C}$  and  $128\text{g S}$  following the change  $\text{C} + \text{S}_2 \rightarrow \text{CS}_2$ ;  $\Delta H = 22 \text{ kCal}$
- (1)  $22 \text{ kCal}$
  - (2)  $11 \text{ kCal}$
  - (3)  $44 \text{ kCal}$
  - (4)  $32 \text{ kCal}$

101. Consider the reaction  $3\text{O}_2 \rightarrow 2\text{O}_3$ ;  $\Delta H = +Ve$ , from the reaction, we can say that :-
- (1) Ozone is more stable than oxygen
  - (2) Ozone is less stable than oxygen and ozone decomposes forming oxygen readily
  - (3) Oxygen is less stable than ozone and oxygen decomposes forming ozone readily
  - (4) None of the above

102. From the reaction  $\text{P}(\text{White}) \rightarrow \text{P}(\text{Red})$ ;  $\Delta H = -18.4 \text{ kJ}$ , it follows that :-
- (1) Red P is readily formed from white P
  - (2) White P is readily formed from red P
  - (3) White P can not be converted to red P
  - (4) White P can be converted into red P and red P is more stable



## FACTORS AFFECTING HEAT OF REACTION

**103.** In Kirchoff's equation which factor affects the heat of reaction :

- (1) Pressure
- (2) Temperature
- (3) Volume
- (4) Atomicity

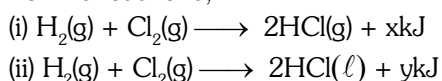
**104.** For the reaction;  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell)$ ,  $\Delta C_p = 7.63 \text{ Cal deg}$ ;  $\Delta H_{25^\circ\text{C}} = 68.3 \text{ kCal}$ , what will be the value (in kCal) of  $\Delta H$  at  $100^\circ\text{C}$  :

- (1)  $7.63 \times (373 - 298) - 68.3$
- (2)  $7.63 \times 10^{-3} (373 - 298) - 68.3$
- (3)  $7.63 \times 10^{-3} (373 - 298) + 68.3$
- (4)  $7.63 \times (373 - 298) + 68.3$

**105.** The enthalpy of a reaction at  $273 \text{ K}$  is  $-3.57 \text{ kJ}$ . what will be the enthalpy of reaction at  $373 \text{ K}$  if  $\Delta C_p = \text{zero}$  :-

- (1)  $-3.57$
- (2) Zero
- (3)  $-3.57 \times \frac{373}{273}$
- (4)  $-375$

**106.** For the reactions,



Which one of the following statement is correct :

- (1)  $x > y$
- (2)  $x < y$
- (3)  $x = y$
- (4) More data required

## HEAT OF FORMATION

**107.** Since the enthalpy of the elements in their standard states is taken to be zero. The heat of formation ( $\Delta H_f$ ) of compounds :

- (1) Is always negative
- (2) Is always positive
- (3) Is zero
- (4) May be positive or negative

**108.** Reaction  $\text{H}_2(\text{s}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}$ ;  $\Delta H = 12.40 \text{ kCal}$ . According to this, heat of formation of HI will be -

- (1)  $12.40 \text{ kCal}$
- (2)  $-12.40 \text{ kCal}$
- (3)  $-6.20 \text{ kCal}$
- (4)  $6.20 \text{ kCal}$

**109.** At  $300\text{K}$  the standard enthalpies of formation of  $\text{C}_6\text{H}_5\text{COOH}(\text{s})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\ell)$  are  $-408$ ,  $-393$  and  $-286 \text{ kJ mol}^{-1}$  respectively. Calculate the heat of combustion of benzoic acid at constant volume :

- (1)  $+3201 \text{ kJ}$
- (2)  $+3199.75 \text{ kJ}$
- (3)  $-3201 \text{ kJ}$
- (4)  $-3199.75 \text{ kJ}$

**110.** Enthalpy of a compound is equal to its :- (When it is formed from constituent particles)

- (1) Heat of combustion
- (2) Heat of formation
- (3) Heat of reaction
- (4) Heat of solution

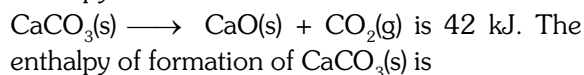
**111.** Which of the following equations represents standard heat of formation of  $\text{CH}_4$  ?

- (1)  $\text{C}_{(\text{diamond})} + 2\text{H}_{2(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
- (2)  $\text{C}_{(\text{graphite})} + 2\text{H}_{2(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
- (3)  $\text{C}_{(\text{diamond})} + 4\text{H}_{(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
- (4)  $\text{C}_{(\text{graphite})} + 4\text{H}_{(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$

**112.** The enthalpy of formation of ammonia is  $-46.0 \text{ kJ mol}^{-1}$ . The enthalpy change for the reaction  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  is :

- (1)  $46.0 \text{ kJ mol}^{-1}$
- (2)  $92.0 \text{ kJ mol}^{-1}$
- (3)  $-23.0 \text{ kJ mol}^{-1}$
- (4)  $-92.0 \text{ kJ mol}^{-1}$

**113.** Given enthalpy of formation of  $\text{CO}_2(\text{g})$  and  $\text{CaO}(\text{s})$  are  $-94.0 \text{ kJ}$  and  $-152 \text{ kJ}$  respectively and the enthalpy of the reaction :



- (1)  $-42 \text{ KJ}$
- (2)  $-202 \text{ KJ}$
- (3)  $+202 \text{ KJ}$
- (4)  $-288 \text{ KJ}$

**114.** Given that standard heat enthalpy of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_8$  are  $-17.9$ ,  $12.5$ ,  $-24.8 \text{ kCal mol}^{-1}$ . The  $\Delta H$  for  $\text{CH}_4 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_8$  is :

- (1)  $-55.2 \text{ kCal}$
- (2)  $-30.2 \text{ kCal}$
- (3)  $55.2 \text{ kCal}$
- (4)  $-19.4 \text{ kCal}$

**115.** The standard molar heat of formation of ethane,  $\text{CO}_2$  and water( $\ell$ ) are respectively  $-21.1$ ,  $-94.1$  and  $-68.3 \text{ kCal}$ . The standard molar heat of combustion of ethane will be

- (1)  $-372 \text{ kCal}$
- (2)  $-162 \text{ kCal}$
- (3)  $-240 \text{ kCal}$
- (4)  $-183.5 \text{ kCal}$

**116.** Two atoms of hydrogen combine to form a molecule of hydrogen gas, the energy of the  $\text{H}_2$  molecule is :

- (1) Greater than that of separate atoms
- (2) Equal to that of separate atoms
- (3) Lower than that of separate atoms
- (4) Some times lower and some times higher

**117.** The  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8 \text{ kJ mol}^{-1}$  respectively the standard enthalpy change (in kJ) for the reaction  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$  is -

- (1)  $524.1$
- (2)  $41.2$
- (3)  $-262.5$
- (4)  $-41.2$



- 118.** The enthalpies of combustion of carbon and carbon monoxide are  $-393.5 \text{ kJ}$  and  $-283 \text{ kJ}$ , respectively the enthalpy of formation of carbon monoxide is :  
 (1)  $-676.5 \text{ kJ}$  (2)  $-110.5 \text{ kJ}$   
 (3)  $110.5 \text{ kJ}$  (4)  $676.5 \text{ kJ}$

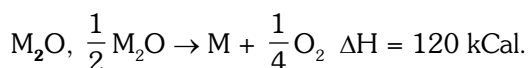
- 119.** The standard heat of formation of  $\text{CS}_2(\ell)$  will be; given that the standard heat of combustion of carbon (s), sulphur(s) and  $\text{CS}_2(\ell)$  are  $-393.3$ ,  $-293.72$  and  $-1108.76 \text{ kJ mol}^{-1}$  respectively is  
 (1)  $-128.02 \text{ kJ mole}^{-1}$   
 (2)  $+12.802 \text{ kJ mol}^{-1}$   
 (3)  $+128.02 \text{ kJ mol}^{-1}$   
 (4)  $-12.802 \text{ kJ mol}^{-1}$

- 120.** The heat of combustion of  $\text{CH}_4(\text{g})$ ,  $\text{C}(\text{s})$  and  $\text{H}_2(\text{g})$  at  $25^\circ\text{C}$  are  $-212.4 \text{ K Cal}$ ,  $-94.0 \text{ K Cal}$  and  $-68.4 \text{ K Cal}$  respectively, the heat of formation of  $\text{CH}_4$  will be -  
 (1)  $+54.4 \text{ K Cal}$  (2)  $-18.4 \text{ K Cal}$   
 (3)  $-375.2 \text{ K Cal}$  (4)  $+212.8 \text{ K Cal}$

- 121.** Standard enthalpy of formation is zero for .  
 (1)  $\text{C}_{\text{diamond}}$  (2)  $\text{Br}_{(\text{g})}$   
 (3)  $\text{C}_{\text{graphite}}$  (4)  $\text{O}_{3(\text{g})}$

- 122.** The standard heats of formation of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  are  $8.0$  and  $2.0 \text{ kCal mol}^{-1}$  respectively the heat of dimerization of  $\text{NO}_2$  in  $\text{kCal}$  is  
 (1)  $10.0$  (2)  $-6.0$  (3)  $-12.0$  (4)  $-14.0$

- 123.** M is a metal that forms an oxide



When a sample of metal M reacts with one mole of oxygen what will be the  $\Delta H$  in that case

- (1)  $240 \text{ kCal.}$  (2)  $-240 \text{ kCal.}$   
 (3)  $480 \text{ kCal.}$  (4)  $-480 \text{ kCal.}$

### HEAT OF COMBUSTION

- 124.** According to equation,  
 $\text{C}_6\text{H}_6(\ell) + 15/2 \text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell);$   
 $\Delta H = -3264.4 \text{ kJ mol}^{-1}$  the energy evolved when  $7.8 \text{ g}$  benzene is burnt in air will be -  
 (1)  $163.22 \text{ kJ}$  (2)  $32.64 \text{ kJ}$   
 (3)  $3.264 \text{ kJ}$  (4)  $326.4 \text{ kJ}$

- 125.** Heat of combustion of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  gases are  $-212.8$ ,  $-373.0$ ,  $-337.0$  and  $-310.5 \text{ kCal}$  respectively at the same temperature. The best fuel among these gases is :  
 (1)  $\text{CH}_4$  (2)  $\text{C}_2\text{H}_6$  (3)  $\text{C}_2\text{H}_4$  (4)  $\text{C}_2\text{H}_2$

- 126.** Given standard enthalpy of formation of  $\text{CO}$  ( $-110 \text{ kJ mol}^{-1}$ ) and  $\text{CO}_2$  ( $-394 \text{ kJ mol}^{-1}$ ). The heat of combustion when one mole of graphite burns is

- (1)  $-110 \text{ kJ}$  (2)  $-284 \text{ kJ}$   
 (3)  $-394 \text{ kJ}$  (4)  $-504 \text{ kJ}$

- 127.** The enthalpy of formation for  $\text{C}_2\text{H}_4(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\ell)$  at  $25^\circ\text{C}$  and  $1 \text{ atm.}$  pressure are  $52$ ,  $-394$  and  $-286 \text{ kJ mole}^{-1}$  respectively. The enthalpy of combustion of  $\text{C}_2\text{H}_4$  will be:-

- (1)  $+1412 \text{ kJ mole}^{-1}$  (2)  $-1412 \text{ kJ mole}^{-1}$   
 (3)  $+142.2 \text{ kJ mole}^{-1}$  (4)  $-141.2 \text{ kJ mole}^{-1}$

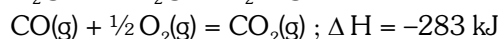
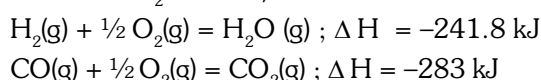
- 128.** The heat of combustion of carbon and carbon monoxide are  $-394$  and  $-285 \text{ kJ mol}^{-1}$  respectively. The heat of formation of  $\text{CO}$  in  $\text{kJ mol}^{-1}$  is:-

- (1)  $+109$  (2)  $-109$   
 (3)  $+218$  (4)  $-218$

- 129.** If heat of combustion of ethylene is  $1411 \text{ kJ}$  when a certain amount of ethylene was burnt  $6226 \text{ kJ}$  heat was evolved. Then the volume of  $\text{O}_2$  (at NTP) that entered into the reaction is :-

- (1)  $296.5 \text{ ml}$  (2)  $296.5 \text{ litre}$   
 (3)  $6226 \times 22.4 \text{ litre}$  (4)  $22.4 \text{ litre}$

- 130.** The heat evolved during the combustion of  $112 \text{ litre}$  of water gas at STP (mixture of equal volume of  $\text{H}_2$  and  $\text{CO}$ ) is : Given



- (1)  $241.8 \text{ kJ}$  (2)  $283 \text{ kJ}$   
 (3)  $1312 \text{ kJ}$  (4)  $1586 \text{ kJ}$

- 131.** A person requires  $2870 \text{ kCal}$  of energy to lead normal daily life. If heat of combustion of cane sugar is  $-1349 \text{ kCal}$ , then his daily consumption of sugar is :

- (1)  $728 \text{ g}$  (2)  $0.728 \text{ g}$   
 (3)  $342 \text{ g}$  (4)  $0.342 \text{ g}$

- 132.** On complete combustion of  $2 \text{ gm}$  methane  $26575 \text{ Cal}$  heat is generated. The heat of formation of methane will be (given heat of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are  $-97000$  and  $-68000 \text{ Cal}$  respectively) :

- (1)  $+20400 \text{ Cal}$  (2)  $+20600 \text{ Cal}$   
 (3)  $-20400 \text{ Cal}$  (4)  $-2000 \text{ Cal}$



**133.** X gm of ethanal was subjected to combustion in a bomb calorimeter and the heat produced is Y Joules. Then -

(1)  $\Delta E_{(\text{combustion})} = -XJ$

(2)  $\Delta E_{(\text{combustion})} = -YJ$

(3)  $\Delta E_{(\text{combustion})} = -\frac{44Y}{X} \text{ J mol}^{-1}$

(4)  $\Delta H_{(\text{combustion})} = -\frac{44Y}{X} \text{ J mol}^{-1}$

**134.** The following are the heats of reactions -

(i)  $\Delta H_f^\circ$  of  $\text{H}_2\text{O}_{(l)} = -68.3 \text{ kCal mol}^{-1}$

(ii)  $\Delta H_{\text{comb.}}^\circ$  of  $\text{C}_2\text{H}_2 = -337.2 \text{ kCal mol}^{-1}$

(iii)  $\Delta H_{\text{comb.}}^\circ$  of  $\text{C}_2\text{H}_4 = -363.7 \text{ kCal mol}^{-1}$

Then heat change for the reaction  $\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$  is -

(1)  $-716.1 \text{ kCal}$  (2)  $+ 337.2 \text{ kCal}$

(3)  $-41.8 \text{ kCal}$  (4)  $-579.5 \text{ kCal}$

**135.** The heat of combustion of a substance is :-

(1) Always positive

(2) Always negative

(3) Numerically equal to the heat of formation

(4) 1 and 3 both

**136.** The value of  $\Delta H$  for the combustion of  $\text{C(s)}$  is  $-94.4 \text{ kCal}$ . The heat of formation of  $\text{CO}_2(\text{g})$  is :-

(1)  $-49.5 \text{ kCal}$  (2)  $-94.4 \text{ kCal}$

(3)  $-188.0 \text{ kCal}$  (4) More data required

**137.** In the combustion of 0.4 g. of  $\text{CH}_4$ , 0.25 kCal. of heat is liberated. The heat of combustion of  $\text{CH}_4$  is

(1)  $-20 \text{ kCal}$  (2)  $-10 \text{ kCal}$

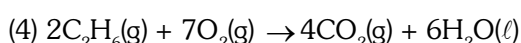
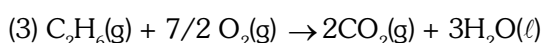
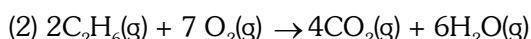
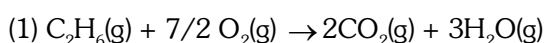
(3)  $-2.5 \text{ kCal}$  (4)  $-5 \text{ kCal}$

**138.** If  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 9\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ ;  $\Delta H = -680 \text{ kCal}$  The weight of  $\text{CO}_2(\text{g})$  produced when 170 kCal of heat is evolved in the combustion of glucose is:-

(1) 265 g (2) 66 g

(3) 11 g (4) 64 g

**139.** Which of the following equations corresponds to the enthalpy of combustion at 298 K :-



**140.** Heat of formation of  $\text{CO}_2$  is  $-94.0 \text{ kCal}$ . What would be the quantity of heat liberated, when 3 g of graphite is burnt in excess of oxygen:-

(1) 23.5 kCal

(2) 2.35 kCal

(3) 94.0 kCal

(4) 31.3 kCal

### HEAT OF NEUTRALIZATION

**141.** The amount of heat liberated when one mole of  $\text{NH}_4\text{OH}$  reacts with one mole of  $\text{HCl}$  is

(1) 13.7 kCal

(2) More than 13.7 kCal

(3) Less than 13.7 kCal

(4) Cannot be predicted

**142.** If  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O} + 13.7 \text{ kCal}$ , then heat of complete neutralisation of one gram mole of  $\text{H}_2\text{SO}_4$  with strong base will be :

(1) 13.7 Kcal

(2) 27.4 Kcal

(3) 6.85 Kcal

(4) 3.425 KCal

**143.** Heat of neutralisation of a strong dibasic acid in dilute solution by  $\text{NaOH}$  is nearly :

(1)  $-27.4 \text{ kCal eq}^{-1}$

(2)  $-13.7 \text{ kCal eq}^{-1}$

(3)  $13.7 \text{ kCal eq}^{-1}$

(4)  $-13.7 \text{ kCal mol}^{-1}$

**144.** The temperature of a 5 ml of strong acid increases by  $5^\circ\text{C}$  when 5 ml of a strong base is added to it. If 10 ml of each are mixed temperature should increase by :

(1)  $5^\circ\text{C}$

(2)  $10^\circ\text{C}$

(3)  $15^\circ\text{C}$

(4) Cannot be known

**145.** The heat of neutralization of  $\text{HCl}$  by  $\text{NaOH}$  is  $-55.9 \text{ kCal mol}^{-1}$ . If the heat of neutralization of  $\text{HCN}$  by  $\text{NaOH}$  is  $-12.1 \text{ kCal mol}^{-1}$ . The energy of dissociation of  $\text{HCN}$  is

(1)  $-43.8 \text{ kJ}$

(2) 43.8 kJ

(3) 68 kJ

(4)  $-68 \text{ kJ}$

**146.** If water is formed from  $\text{H}^+$  ions and  $\text{OH}^-$  the heat of formation of water is :

(1)  $-13.7 \text{ kCal}$

(2) 13.7 kCal

(3)  $-63.4 \text{ kCal}$

(4) More data required

**147.** The change in the enthalpy of



(1) Heat of neutralisation (2) Heat of reaction

(3) Heat of hydration

(4) Heat of solution

**148.** Heat of neutralisation of oxalic acid is  $-106.7 \text{ kJ mol}^{-1}$  using  $\text{NaOH}$  hence  $\Delta H$  of :



(1)  $5.88 \text{ kJ mol}^{-1}$

(2)  $-5.88 \text{ kJ mol}^{-1}$

(3)  $-13.7 \text{ kCal mol}^{-1}$

(4)  $7.5 \text{ kJ mol}^{-1}$



### HEAT OF HYDROGENATION

- 149.** The heat of combustion of  $C_2H_4$ ,  $C_2H_6$  and  $H_2$  are  $-1409.5$  kJ,  $-1558.3$  kJ and  $-285.6$  kJ. The heat of hydrogenation of ethene is -  
(1)  $-136.8$  kJ (2)  $-13.68$  kJ  
(3)  $273.6$  kJ (4)  $1.368$  kJ
- 150.** The enthalpy of combustion of cyclohexane, cyclohexene and  $H_2$  are respectively  $-3920$ ,  $-3800$  and  $-241$  kJ  $mol^{-1}$ . The heat of hydrogenation of cyclohexene is:-  
(1)  $-121$  kJ  $mol^{-1}$  (2)  $121$  kJ  $mol^{-1}$   
(3)  $-242$  kJ  $mol^{-1}$  (4)  $242$  kJ  $mol^{-1}$

### BOND ENERGY/RESONANCE ENERGY

- 151.** Bond energy of a molecule :  
(1) Is always negative  
(2) Is always positive  
(3) Either positive or negative  
(4) Depends upon the physical state of the system
- 152.** Among the following for which reaction heat of reaction represents bond energy of HCl  
(1)  $HCl(g) \longrightarrow H^+(g) + Cl^-(g)$   
(2)  $HCl(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g)$   
(3)  $2HCl(g) \longrightarrow H_2(g) + Cl_2(g)$   
(4)  $HCl(g) \longrightarrow H(g) + Cl(g)$
- 153.** The bond energies of  $F_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$  are  $155.4$ ,  $243.6$ ,  $193.2$  and  $151.2$  kJ  $mol^{-1}$  respectively. The strongest bond is :  
(1)  $F - F$  (2)  $Cl - Cl$   
(3)  $Br - Br$  (4)  $I - I$
- 154.** Energy required to dissociate 4g of gaseous hydrogen into free gaseous atoms is 208 kCal at  $25^\circ C$ . The bond energy of  $H-H$  bond will be :  
(1)  $1.04$  kCal (2)  $10.4$  kCal  
(3)  $104$  kCal (4)  $1040$  kCal
- 155.** Heat evolved in the reaction  $H_2 + Cl_2 \longrightarrow 2HCl$  is 182 kJ. Bond energies of  $H-H$  and  $Cl-Cl$  are 430 and 242 kJ  $mol^{-1}$  respectively. The  $H-Cl$  bond energy is :  
(1)  $245$  kJ  $mol^{-1}$   
(2)  $427$  kJ  $mol^{-1}$   
(3)  $336$  kJ  $mol^{-1}$   
(4)  $154$  kJ  $mol^{-1}$

- 156.** The enthalpy change for the reaction  $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$  is..... . The bond energies are,  
 $H-H = 103$ ,  $C-H = 99$ ,  $C-C = 80$  &  $C=C = 145$  kCal  $mol^{-1}$   
(1)  $-10$  kCal  $mol^{-1}$  (2)  $+10$  kCal  $mol^{-1}$   
(3)  $-30$  kCal  $mol^{-1}$  (4)  $+30$  kCal  $mol^{-1}$
- 157.** Bond dissociation enthalpies of  $H_2(g)$  and  $N_2(g)$  are  $436.0$  kJ  $mol^{-1}$  and  $941.8$  kJ  $mol^{-1}$  respectively and enthalpy of formation of  $NH_3(g)$  is  $-46$  kJ  $mol^{-1}$ . What is enthalpy of atomization of  $NH_3(g)$  ?  
(1)  $390.3$  kJ  $mol^{-1}$  (2)  $1170.9$  kJ  $mol^{-1}$   
(3)  $590$  kJ  $mol^{-1}$  (4)  $720$  kJ  $mol^{-1}$
- 158.** From the reactions :  
 $C(s) + 2H_2(g) \rightarrow CH_4(g)$   $\Delta H = -X$  Kcal  
 $C(g) + 4H(g) \rightarrow CH_4(g)$ ,  $\Delta H = -X_1$  Kcal  
 $CH_4(g) \rightarrow CH_3(g) + H(g)$   $\Delta H = +Y$  (Kcal)  
Bond energy of  $C-H$  bond is -  
(1)  $\frac{X}{4}$  kCal  $mol^{-1}$   
(2)  $Y$  kCal  $mol^{-1}$   
(3)  $\frac{X_1}{4}$  kCal  $mol^{-1}$   
(4)  $X_1$  kCal  $mol^{-1}$
- 159.** The enthalpy changes at 298 K in successive breaking of  $O-H$  bonds of water are  
 $H_2O \longrightarrow H(g) + OH(g)$ ;  $\Delta H = 498$  kJ  $mol^{-1}$   
 $OH(g) \longrightarrow H(g) + O(g)$ ;  $\Delta H = 428$  kJ  $mol^{-1}$   
the bond enthalpy of  $O-H$  bond is  
(1)  $498$  kJ  $mol^{-1}$  (2)  $428$  kJ  $mol^{-1}$   
(3)  $70$  kJ  $mol^{-1}$  (4)  $463$  kJ  $mol^{-1}$
- 160.** If  $\Delta H_f^\circ$  of  $ICl_{(g)}$ ,  $Cl_{(g)}$ , and  $I_{(g)}$  is  $17.57$ ,  $121.34$  and  $106.96$  J  $mol^{-1}$  respectively. Then bond dissociation energy of  $ICl$  bond is -  
(1)  $35.15$  J  $mol^{-1}$  (2)  $106.69$  J  $mol^{-1}$   
(3)  $210.73$  J  $mol^{-1}$  (4)  $420.9$  J  $mol^{-1}$
- 161.** Heat of dissociation of benzene to elements is  $5535$  kJ  $mol^{-1}$ . The bond enthalpies of  $C-C$ ,  $C=C$  and  $C-H$  are  $347.3$ ,  $615.0$  and  $416.2$  kJ respectively. Magnitude resonance energy of benzene is  
(1)  $1.51$  kJ (2)  $15.1$  kJ  
(3)  $151$  kJ (4)  $1511$  kJ





## SOME OTHER HEAT OF REACTIONS

- 162.** The enthalpy change for the reaction  $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$  is called  
 (1) Enthalpy of formation  
 (2) Enthalpy of combustion  
 (3) Enthalpy of hydrogenation  
 (4) Enthalpy of vaporisation
- 163.**  $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g})$ , In this process value of  $\Delta H$  will be -  
 (1) Positive  
 (2) Negative  
 (3) Zero  
 (4) Nothing can be predicted
- 164.** The magnitude of heat of solution ..... on addition of solvent to solution  
 (1) Decreases  
 (2) Increases  
 (3) Remains constant  
 (4) Increases or decreases
- 165.** If  $\text{H}_2(\text{g}) = 2\text{H}(\text{g})$ ;  $\Delta H = 104 \text{ kCal}$ , than heat of atomisation of hydrogen is :  
 (1) 52 kCal (2) 104 kCal  
 (3) 208 kCal (4) None of these
- 166.**  $\text{S}_{(\text{rhombic})} + \text{O}_{2(\text{g})} \longrightarrow \text{SO}_{2(\text{g})}$ ;  $\Delta H = -297.5 \text{ kJ}$   
 $\text{S}_{(\text{monoclinic})} + \text{O}_{2(\text{g})} \longrightarrow \text{SO}_2$ ;  $\Delta H = -300 \text{ kJ}$   
 The data can predict that -  
 (1) Rhombic sulphur is yellow in colour  
 (2) Monoclinic sulphur has metallic lusture.  
 (3) Monoclinic sulphur is more stable  
 (4)  $\Delta H$  transition of  $\text{S}_R$  to  $\text{S}_M$  is endothermic
- 167.** The heat of combustion of yellow phosphorous and red phosphorous are  $-9.91 \text{ kJ}$  and  $-8.78 \text{ kJ}$  respectively. The heat of transition of yellow phosphorous to red phosphorous is  
 (1)  $-18.69 \text{ kJ}$  (2)  $+1.13 \text{ kJ}$   
 (3)  $+18.69 \text{ kJ}$  (4)  $-1.13 \text{ kJ}$
- 168.** For the change  $\text{C}(\text{diamond}) \longrightarrow \text{C}(\text{graphite})$ ;  $\Delta H = -1.89 \text{ KJ}$ , if 6 g of diamond and 6g of graphite are seperately burnt to yield  $\text{CO}_2$  the heat liberated in first case is :  
 (1) Less than in the second case by 1.89 kJ  
 (2) Less than in the second case by 11.34 kJ  
 (3) Less than in the second case by 14.34 kJ  
 (4) More than in the second case by 0.945 kJ

- 169.**  $2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \longrightarrow 2\text{CO}_{2(\text{g})} + X \text{ kJ}$   
 In the above equation X kJ refers to :  
 (1) Heat of formation of  $\text{CO}_2$   
 (2) Heat of vapourisation  
 (3) Heat of reaction  
 (4) Heat of sublimation
- 170.** Which of the following reactions represents  $\Delta H$  (hydration) :-  
 (1)  $\text{CuSO}_4(\text{s}) + (\text{aq}) \rightarrow \text{CuSO}_4(\text{aq})$ ;  $\Delta H = -x \text{ kJ}$   
 (2)  $\text{BaCl}_2(\text{s}) + 2\text{H}_2\text{O}(\ell) \rightarrow \text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ ;  
 $\Delta H = -x' \text{ kJ}$   
 (3)  $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\ell) + (\text{aq}) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{aq})$ ;  
 $\Delta H = -y' \text{ kJ}$   
 (4) None of the above
- 171.**  $\Delta H$  for the reaction,  $\text{I}_{(\text{g})} + \text{I}_{(\text{g})} \rightarrow \text{I}_{2(\text{g})}$  will be:-  
 (1) Zero (2) -ve (3) +ve (4)  $\infty$
- 172.** Given that :  
 $\text{A}(\text{s}) \rightarrow \text{A}(\ell)$ ;  $\Delta H = x$ ,  $\text{A}(\ell) \rightarrow \text{A}(\text{g}) - y$   
 The heat of sublimation of A will be:-  
 (1)  $x + y$  (2)  $x - y$   
 (3)  $x$  or  $y$  (4)  $-(x + y)$

## HESS LAW

- 173.** The enthalpy change of a reaction does not depend on  
 (1) State of reactants and products  
 (2) Nature of reactants and products  
 (3) Different intermediate reactions  
 (4) Initial and final enthalpy change of reaction
- 174.** From the thermochemical reactions,  
 $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}$ ;  $\Delta H = -110.5 \text{ kJ}$   
 $\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$ ;  $\Delta H = -283.2 \text{ kJ}$   
 the heat of reaction of  $\text{C}(\text{graphite}) + \text{O}_2 \longrightarrow \text{CO}_2$  is :  
 (1) 393.7 kJ  
 (2)  $-393.7 \text{ kJ}$   
 (3)  $-172.7 \text{ kJ}$   
 (4)  $+172.7 \text{ kJ}$
- 175.** If  $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$ ;  $\Delta H = -68.39 \text{ kCal}$   
 $\text{K} + \text{H}_2\text{O} + \text{water} \longrightarrow \text{KOH}(\text{aq}) + \frac{1}{2}\text{H}_2$ ;  $\Delta H = -48.0 \text{ kCal}$   
 $\text{KOH} + \text{water} \longrightarrow \text{KOH}(\text{aq})$   $\Delta H = -14.0 \text{ kCal}$   
 the heat of formation of KOH is -  
 (1)  $-68.39 + 48 - 14.0$   
 (2)  $-68.39 - 48.0 + 14.0$   
 (3)  $+68.39 - 48.0 + 14.0$   
 (4)  $+68.39 + 48.0 - 14.0$

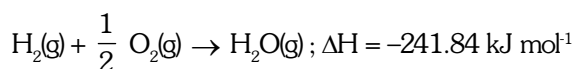
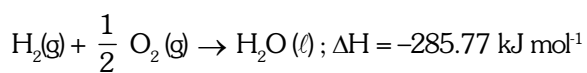


- 176.** Given  $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 94.2 \text{ kCal}$   
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) + 68.3 \text{ kCal}$   
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 210.8 \text{ kCal}$   
 The heat of formation of methane in Kcal will be  
 (1) -45.9 (2) -47.8  
 (3) -20.0 (4) -47.3
- 177.** From the following data, the heat of formation of  $\text{Ca(OH)}_2(\text{s})$  at  $18^\circ\text{C}$  is ..... kCal.  
 (i)  $\text{CaO(s)} + \text{H}_2\text{O}(\ell) = \text{Ca(OH)}_2(\text{s})$  ;  
 $\Delta H_{18^\circ\text{C}} = -15.26 \text{ kCal} \dots\dots$   
 (ii)  $\text{H}_2\text{O}(\ell) = \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  ;  
 $\Delta H_{18^\circ\text{C}} = 68.37 \text{ kCal} \dots\dots$   
 (iii)  $\text{Ca(s)} + \frac{1}{2}\text{O}_2(\text{g}) = \text{CaO(s)}$  ;  
 $\Delta H_{18^\circ\text{C}} = -151.80 \text{ kCal} \dots\dots$   
 (1) -98.69 (2) -235.43  
 (3) 194.91 (4) 98.69
- 178.** If,  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl(g)} ; \Delta H^\circ = -44 \text{ kCal}$   
 $2\text{Na(s)} + 2\text{HCl(g)} \longrightarrow 2\text{NaCl(s)} + \text{H}_2(\text{g})$ ;  
 $\Delta H = -152 \text{ kCal}$   
 Then,  $\text{Na(s)} + 0.5 \text{ Cl}_2(\text{g}) \longrightarrow \text{NaCl(s)} ; \Delta H^\circ = ?$   
 (1) 108 kCal (2) 196 kCal  
 (3) -98 kCal (4) 54 kCal
- 179.** (i)  $\text{S(s)} + 3/2 \text{ O}_2(\text{g}) = \text{SO}_3(\text{g}) + 2x \text{ kCal}$   
 (ii)  $\text{SO}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) = \text{SO}_3(\text{g}) + y \text{ kCal}$   
 Calculate the heat of formation of  $\text{SO}_2$  :  
 (1)  $(2x + y)$  (2)  $-(2x - y)$   
 (3)  $x + y$  (4)  $2x / y$
- 180.** If  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$  ;  $\Delta H = -298.2$   
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$  ;  $\Delta H = -98.7$   
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$  ;  $\Delta H = -130.2$   
 $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$  ;  $\Delta H = -287.3$   
 Then the enthalpy of formation of  $\text{H}_2\text{SO}_4$  at  $298 \text{ K}$  is -  
 (1) -814.4 kJ (2) -650.3 kJ  
 (3) -320.5 kJ (4) -433.5 kJ
- 181.** Given that :  
 $\text{Zn} + \frac{1}{2}\text{O}_2 \rightarrow \text{ZnO} + 84000 \text{ Cal} \dots\dots\dots 1$   
 $\text{Hg} + \frac{1}{2}\text{O}_2 \rightarrow \text{HgO} + 21700 \text{ Cal} \dots\dots\dots 2$   
 The heat of reaction ( $\Delta H$ ) for,  
 $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$  is :-  
 (1) 105700 Cal  
 (2) 62300 Cal  
 (3) -105700 Cal  
 (4) -62300 Cal

- 182.** Given that -  
 $2\text{C(s)} + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) \quad \Delta H = -787 \text{ kJ}$   
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -286 \text{ kJ}$   
 $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \quad \Delta H = -1310 \text{ kJ}$   
 Heat of formation of acetylene is :-  
 (1) + 1802 kJ (2) - 1802 kJ  
 (3) - 800 kJ (4) + 237 kJ
- 183.** Find the heat change in the reaction :  
 $\text{NH}_3(\text{g}) + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$   
 from the following data  
 $\text{NH}_3(\text{g}) + \text{aq} \rightarrow \text{NH}_3(\text{aq}), \quad \Delta H = -8.4 \text{ kCal}$   
 $\text{HCl(g)} + \text{aq} \rightarrow \text{HCl(aq)}, \quad \Delta H = -17.3 \text{ kCal}$   
 $\text{NH}_3(\text{aq}) + \text{HCl(aq)} \rightarrow \text{NH}_4\text{Cl(aq)}, \Delta H = -12.5 \text{ kCal}$   
 $\text{NH}_4\text{Cl(s)} + \text{aq} \rightarrow \text{NH}_4\text{Cl(aq)}, \Delta H = +3.9 \text{ kCal}$   
 (1) - 42.1 (2) - 34.3  
 (3) + 34.3 (4) + 42.1
- 184.** The heat of reaction for  
 $\text{A} + \frac{1}{2}\text{O}_2 \rightarrow \text{AO}$  is - 50 kCal and  
 $\text{AO} + \frac{1}{2}\text{O}_2 \rightarrow \text{AO}_2$  is 100 kCal. The heat of  
 reaction for  $\text{A} + \text{O}_2 \rightarrow \text{AO}_2$  is:-  
 (1) - 50 kCal (2) + 50 kCal  
 (3) 100 kCal (4) 150 kCal
- 185.**  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 94.0 \text{ kCal}$   
 $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}), \quad \Delta H = -67.7 \text{ kCal}$   
 from the above reactions find how much heat  
 ( $\text{kCal mole}^{-1}$ ) would be produced in the following  
 reaction:  $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$   
 (1) 20.6 (2) 26.3  
 (3) 44.2 (4) 161.6
- 186.** Using the following thermochemical data:  
 $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}), \quad \Delta H = -94.0 \text{ kCal}$   
 $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell), \Delta H = -68.0 \text{ kCal}$   
 $\text{CH}_3\text{COOH}(\ell) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell), \Delta H = -210.0 \text{ kCal}$   
 The heat of formation of acetic acid is:-  
 (1) 116.0 kCal (2) - 116.0 kCal  
 (3) - 114.0 kCal (4) + 114.0 kCal



**187.** The enthalpy of vapourisation of liquid water using the data:



(1) + 43.93 kJ mol<sup>-1</sup>      (2) - 43.93 kJ mol<sup>-1</sup>

(3) + 527.61 kJ mol<sup>-1</sup>      (4) - 527.61 kJ mol<sup>-1</sup>

**188.**  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell); \Delta H_{298\text{K}} = -68.32 \text{ kCal}$ . Heat of vapourisation of water at 1 atm and 25°C is 10.52 kCal. The standard heat of formation (in kCal) of 1 mole of water vapour at 25°C is

(1) 10.52      (2) -78.84

(3) +57.80      (4) -57.80

**189.** The heat of solution of anhydrous  $\text{CuSO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are - 15.89 and 2.80 kCal mol<sup>-1</sup> respectively. What will be the heat of hydration of anhydrous  $\text{CuSO}_4$ ?

(1) -18.69 kCal      (2) 18.69 kCal

(3) -28.96 kCal      (4) 28.96 kCal

**190.** One mole of anhydrous salt AB dissolves in water and liberates 21.0 J mol<sup>-1</sup> of heat. The value of  $\Delta H_{(\text{hydration})}$  of AB is -29.4 J mol<sup>-1</sup>. The heat of dissolution of hydrated salt  $\text{AB} \cdot 2\text{H}_2\text{O}(\text{s})$  is -

(1) 50.4 J mol<sup>-1</sup>

(2) 8.4 J mol<sup>-1</sup>

(3) -50.4 J mol<sup>-1</sup>

(5) -8.4 J mol<sup>-1</sup>

**191.** Which of the following expressions is true:-

(1)  $H_f^0(\text{CO}, \text{g}) = \frac{1}{2} \Delta H_f^0(\text{CO}_2, \text{g})$

(2)  $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_f^0(\text{C}, \text{graphite}) + \frac{1}{2} \Delta H_f^0(\text{O}_2, \text{g})$

(3)  $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_f^0(\text{CO}_2, \text{g}) - \frac{1}{2} \Delta H_f^0(\text{O}_2, \text{g})$

(4)  $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_{\text{comb}}^0(\text{C}, \text{graphite}) - \Delta H_{\text{comb}}^0(\text{CO}, \text{g})$

### EXERCISE-I (Conceptual Questions)

### ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	4	4	3	3	1	4	1	1	1	4	2	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	4	4	1	1	4	3	1	3	2	2	4	2	2	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	1	2	1	1	2	3	4	2	2	2	3	1	4	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	2	3	4	3	4	3	1	1	2	3	1	3	1	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	2	2	1	1	4	2	4	3	2	4	2	1	2	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	3	3	4	4	1	2	2	2	4	1	4	1	4	1
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	1	2	3	1	3	4	1	2	4	3	2	4	2	3	1
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	2	4	4	4	2	2	2	4	4	1	3	2	2	3	2
Que.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
Ans.	3	4	4	4	1	3	2	2	2	3	1	3	3	3	2
Que.	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
Ans.	2	2	2	3	1	3	2	2	1	2	1	1	4	1	1
Que.	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165
Ans.	2	4	2	3	2	3	2	3	4	3	3	1	1	3	2
Que.	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180
Ans.	4	4	4	3	2	2	1	3	2	2	3	2	3	2	1
Que.	181	182	183	184	185	186	187	188	189	190	191				
Ans.	4	4	1	2	2	3	1	4	1	2	4				





## Directions for Assertion &amp; Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.  
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.  
 (C) If Assertion is True but the Reason is False.  
 (D) If both Assertion & Reason are false.

- Assertion :-** There is no reaction known for which  $\Delta G$  is positive, yet it is spontaneous.  
**Reason :-** For photochemical reactions,  $\Delta G$  is negative.  
 (1) A (2) B (3) C (4) D
- Assertion :-** Absolute value of enthalpy cannot be determined.  
**Reason :-** Enthalpy is defined as  $H=E+PV$ , and value of internal energy cannot be determined absolutely therefore absolute value of enthalpy can not be determined.  
 (1) A (2) B (3) C (4) D
- Assertion :-** When a rubber band is stretched entropy increases.  
**Reason :-** During expansion entropy increases.  
 (1) A (2) B (3) C (4) D
- Assertion :-** At constant pressure for the change  $H_2O(s) \rightarrow H_2O(g)$  work done is negative.  
**Reason :-** During phase transition work done is always negative.  
 (1) A (2) B (3) C (4) D
- Assertion :-** Enthalpy of graphite is lower than that of diamond.  
**Reason :-** Entropy of graphite is greater than that of diamond.  
 (1) A (2) B (3) C (4) D
- Assertion :-** The enthalpy of formation of gaseous oxygen molecules at 298K and under a pressure of one atm. is zero.  
**Reason :-** The entropy of formation of gaseous oxygen molecules under the same condition is zero.  
 (1) A (2) B (3) C (4) D
- Assertion :-** Many endothermic reactions that are not spontaneous at room temp. becomes spontaneous at high temp.  
**Reason :-** Entropy of the system increases with increase in temperature.  
 (1) A (2) B (3) C (4) D
- Assertion :-** Mass, Volume and pressure are extensive properties.  
**Reason :-** Extensive properties depend upon the amount of the substance.  
 (1) A (2) B (3) C (4) D
- Assertion :-** For a particular reaction, heat of combustion at constant pressure ( $q_p$ ) is always greater than that at constant volume ( $q_v$ ).  
**Reason :-** Combustion reactions are invariably accomplished by increase in no. of moles.  
 (1) A (2) B (3) C (4) D
- Assertion :-** At constant temp  $0^\circ\text{C}$  and 1atm, the change  $H_2O(s) \rightarrow H_2O(l)$   $\Delta H$  and  $\Delta E$  both are zero.  
**Reason :-** During isothermal process  $H$  and  $E$  both remains constant.  
 (1) A (2) B (3) C (4) D
- Assertion :-** The change in internal energy ( $\Delta E$ ) for the vapourization of one mole of water at 1 atm and 373 K is zero.  
**Reason :-** For all isothermal processes  $\Delta E=0$   
 (1) A (2) B (3) C (4) D
- Assertion:-** Water in liquid state is more stable than ice at room temperature.  
**Reason:-** Water in liquid form has higher entropy than ice.  
 (1) A (2) B (3) C (4) D
- Assertion:-** In an isolated system the entropy increases due to spontaneous process.  
**Reason:-** The processes in an isolated system are isothermal.  
 (1) A (2) B (3) C (4) D
- Assertion :-** Entropy is always constant for a closed system.  
**Reason :-** Closed system is always reversible  
 (1) A (2) B (3) C (4) D



15. **Assertion :-** For an isolated system  $q$  is zero.  
**Reason :-** In an isolated system change in  $U$  is zero.  
 (1) A (2) B (3) C (4) D
16. **Assertion :-** Entropy of system always increases for a spontaneous reaction.  
**Reason :-** Enthalpy of reaction always decreases for spontaneous reaction.  
 (1) A (2) B (3) C (4) D
17. **Assertion :-** Catalyst changes Gibbs free energy of system.  
**Reason :-** Catalyst changes preexponential factor of a chemical reaction.  
 (1) A (2) B (3) C (4) D
18. **Assertion :-** Entropy increases with increase in temperature of gas.  
**Reason :-** If  $q_{rev}$  is same, then entropy of that system is higher for which temperature is higher.  
 (1) A (2) B (3) C (4) D
19. **Assertion :-** The value of specific heat at constant pressure is more than that at constant volume.  
**Reason :-** The energy required to raise temperature by a unit at constant pressure is greater because some amount of heat is used in doing work.  
 (1) A (2) B (3) C (4) D
20. **Assertion :** Sum of two path functions is always path function.  
**Reason :** Sum of path function depends on path followed.  
 (1) A (2) B (3) C (4) D
21. **Assertion :-** Heat is not a state thermodynamic property.  
**Reason :-** Heat given in a process depends on its type.  
 (1) A (2) B (3) C (4) D
22. **Assertion :-** For ideal gas in a closed container with adiabatic walls, temperature decreases when work is done by the system.  
**Reason :-** Internal energy is used in work done by the system.  
 (1) A (2) B (3) C (4) D
23. **Assertion :-** Adiabatic free expansion of an ideal gas is irreversible.  
**Reason :-**  $PV = \text{constant}$  for reversible adiabatic expansion.  
 (1) A (2) B (3) C (4) D
24. **Assertion :-** Internal energy at particular temperature does not depend on volume.  
**Reason :-** State function does not depend on volume.  
 (1) A (2) B (3) C (4) D
25. **Assertion :-** Graphite is thermodynamically most stable allotrope of carbon.  
**Reason :-** Standard heat of formation of graphite is  $+1.9 \text{ kJ/mol}$ .  
 (1) A (2) B (3) C (4) D
26. **Assertion :** A gas expands from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$  the work done in 2 steps will be more than, if the process is carried out in single step.  
**Reason :** Work done is path dependent quantity.  
 (1) A (2) B (3) C (4) D
27. **Assertion :** All spontaneous process in nature are irreversible.  
**Reason :** All reversible process are quasistatic.  
 (1) A (2) B (3) C (4) D
28. **Assertion :-** Sum of  $q$  and  $w$  is different in reversible and irreversible process.  
**Reason :-** Sum of two path function can never state function.  
 (1) A (2) B (3) C (4) D
29. **Assertion :** Internal energy of gas remain constant during adiabatic free expansion.  
**Reason :** Work done is zero and heat exchange is zero.  
 (1) A (2) B (3) C (4) D

### EXERCISE-II(Assertion & Reason)

### ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	1	4	3	2	3	2	4	4	4	4	2	1	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	4	4	3	1	4	1	1	3	3	3	1	2	4	1	

